PROGRAM AND ABSTRACTS

NATO Advanced Research Workshop on

NON-THERMAL PLASMA TECHNIQUES FOR POLLUTION CONTROL

Cambridge University, England
September 21-25, 1992

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Sponsored by

NATO Scientific and Environmental Affairs Division
US Army European Research Office
US Office of Naval Research European Office
ABB - Asea Brown Boveri
Asahi Kogyosha Co. Ltd. (Japan)
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CONTENTS

INDUSTRIAL SCALE TESTS OF FLUE GAS TREATMENT

ELECTRON BEAM PROCESSING

DC DISCHARGE PROCESSING

SILENT DISCHARGE PROCESSING

AC DISCHARGE PROCESSING

PULSED CORONA PROCESSING

FUNDAMENTALS

TECHNOLOGY DEVELOPMENTS

DC DISCHARGE PROCESSING - Addendum

NATO ADVANCED RESEARCH WORKSHOP ON NON-THERMAL PLASMA TECHNIQUES FOR POLLUTION CONTROL

Acid rain, global warming, ozone depletion, and smog...
On September 21-25, 1992, scientists and engineers will meet in Cambridge University to discuss the application of plasma technologies to the solution of these serious environmental pollution problems.

Cambridge University, England | **September 21-25, 1992**

Introduction

Acid rain, global warming, ozone depletion, and smog are preeminent environmental problems facing the world today. Non-thermal plasma techniques offer an innovative approach to the cost-effective solution of these problems. Many potential applications of non-thermal plasmas to air pollution control have already been demonstrated. On Sept. 21-25, 1992, leading experts from academia, government laboratories and in-

Acid rain, global warming, ozone depletion, and smog... Non-thermal plasma techniques offer an innovative approach to the cost-effective solution of these problems.

dustry will meet in Cambridge University, England, to discuss laboratory studies and industrial implementations of non-thermal plasmas for the abatement of hazardous gaseous wastes.

Nitrogen oxides (NO_x) and sulfur dioxide (SO_2), produced primarily by coal-burning power plants and automobile exhaust, are major contributors to acid rain. Carbon dioxide, released in large quantities when fossil fuels like coal, oil and natural gas are burned, is the biggest contributor to the accumulating greenhouse shield. Volatile organic compounds (VOCs), such as chlorofluorocarbons (CFCs) and halons, have been widely used in air-conditioning, refrigeration and aerosol products, and are present in fumes given off by gasoline, paints, and degreasing agents. They are used by the electronics industry as cleaning agents and by the chemical industry in the manufacture of foam products. VOCs are the main threat to the ozone layer, and contribute to chemicals that could lead to global warming. Soot particles and hydrocarbons emitted by cars and trucks are leading contributors to smog pollution. Well-understood conventional technologies do exist for the treatment of some of these toxic gases, but they have practical limitations imposed by cost, energy requirements and by-product disposal. Non-thermal plasma techniques offer the advantages of energy efficiency and the capability for the simultaneous removal of coexisting pollutants.

In devices such as plasma torches, the plasma is used only to create heat, which is applied indiscriminately to all the components of the waste. In the non-thermal plasma approach, the non-equilibrium properties of the plasma are fully exploited. These plasmas are characterized by high electron temperatures, while the gas remains at near ambient temperature and pressure. The energy is directed preferentially to the undesirable components that are often present in very small concentrations. These techniques utilize the dissociation and ionization of the background gas to produce radicals that, in turn, decompose the toxic compounds. For many applications, particularly in the removal of gaseous pollutants, the non-thermal plasma approach would be most appropriate because of its high energy efficiency and its capability for the simultaneous removal of various pollutants. For others, including many

The key to success in the non-thermal plasma approach is to produce a discharge in which the majority of the electrical energy goes into the production of energetic electrons, rather than into gas heating.

mixed waste streams, the best approach might be to use a thermal plasma to incinerate the complete waste, including its container, and to use a non-thermal plasma reactor to clean the off-gases.

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ABOUT THIS WORKSHOP

PREFACE by

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energetic electrons, rather than into gas heating. Even though the electrons are short-lived in atmospheric-pressure discharges, and rarely collide with a pollutant molecule, they undergo many collisions with the dominant nitrogen, oxygen and water molecules. The efficiency of the approach arises from the fact that the radicals (produced by the collisions of these electrons with the background gas) have long lifetimes and react selectively with the contaminant molecules. For example, in a typical application to flue gas cleanup, these electrons produce radicals, such as O and OH, through the dissociation or ionization of molecules such as H_2O or O_2. The object is to make acid rain in the flue gas instead of in the atmosphere. The radicals diffuse through the gas and preferentially oxidize the nitrogen oxides and sulfur oxides to form acids that can then be easily neutralized to form non-toxic, easily-collectible (and commercially salable) compounds.

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Non-thermal plasmas can be created in essentially two different ways: by electron-beam irradiation, and by electrical discharges.

Electron-Beam Irradiation

From the results obtained by basic studies and pilot-plant tests that have been done in Japan, Germany, Poland, and the USA, the process is considered to have an excellent potential for the simultaneous removal of NO_x/SO_2 without producing the reaction end waste products encountered in conventional absorption treatment.

Electron-beam irradiation has been proven to be an effective method for removing nitrogen oxides and sulfur dioxide in flue gases from industrial plants such as power stations and steel plants. In this method, the energy of the electron beam is used directly to dissociate and ionize the background gas. During the ionization by the beam, a shower of secondary electrons is produced, which further produce a cascade of ionization and dissociation. This cascading effect produces a large volume of plasma that can be used to initiate the conversions of NO_x and SO_2 to aerosols that can be collected by electrostatic precipitators or by bag filters. From the results obtained by basic studies and pilot-plant tests that have been done in Japan, Germany, Poland, and the USA, the process is considered to have an excellent potential for the simultaneous removal of NO_x/SO_2 without producing the reaction end waste products encountered in conventional absorption treatment. In Japan, the development of this process has been a result of the joint effort since 1970 by the Ebara Corporation (Kawamura et al. 1972), the Japan Atomic Energy Research Institute (Tokunaga et al. 1984), and Nippon Steel. In the USA, the evaluation of this process has been conducted by the Ebara Environmental Corporation (Frank et al. 1990) and Research-Cottrell (Helfritch et al. 1984), with support from the US Department of Energy. In Germany, pilot-plant studies have been performed at the Nuclear Research Center, the University of Karlsruhe, and Badenwerk (Willibald et al. 1990) (Platzer et al. 1990) (Jordan 1990). In Poland, a demonstration facility has been in operation at the Institute of Nuclear Chemistry and Technology in Warsaw. In Russia, several programs on electron-beam irradiation of flue gases are underway in Moscow at the Institute of Chemical Physics (Shvedchikov et al. 1988) and the Kurchatov Institute of Atomic Energy (Baranchicov et al. 1992).

Three advanced pilot plant tests are now being conducted for electron-beam treatment of flue gas in Japan.

...testing is being done to optimize ... exhaust gas treatment system in a vehicle tunnel under Tokyo Bay.

Three advanced pilot plant tests are now being conducted for electron-beam treatment of flue gas in Japan (Maezawa et al. 1992). At the Ebara Corporation research facility in Fujisawa, the electron-beam process is being fine tuned for commercial use, and testing is being performed on incinerator gases and diesel truck exhaust gases. At the Chubu Electric Plant facility in Nagoya, the installation has its own boiler and can adjust the pollutant concentration of the flow gas, with studies focused on process optimization, equipment reliability, and by-product handling. At the Tokyo

Metropolitan tunnel facility, testing is being done to optimize a high-flow, low-NO_x-concentration exhaust gas treatment system in a vehicle tunnel under Tokyo Bay. In addition, the gases are analyzed for other hydrocarbons to determine the effects of the electron-beam process on unburned hydrocarbons. Electron-beam irradiation is now also being applied to the treatment of other types of hazardous emissions. In Germany, experiments are being conducted in Karlsruhe (Paur 1992) and by Asea Brown Boveri in Heidelberg (Esrom et al. 1992), to determine the removal efficiencies and energy consumption of electron-beam-induced cleaning of dilute emissions of volatile organic compounds.

Electron-beam irradiation is now also being applied to the treatment of ... volatile organic compounds.

The high capital cost of accelerators and x-ray hazard associated with electron-beam pollution control systems have motivated studies into alternate plasma-based technologies such as those utilizing electrical discharges. Electrical discharges can be produced in many different forms, depending on the geometry of the reactor and the electrical power supply. Many reactor designs use electrodes, such as small diameter wires, needles or sharp edged metals, that promote strong electric fields. The reactors are driven by direct current (DC), alternating current (AC), or pulsed power sources.

Pulsed Corona

One type of discharge reactor that has shown very promising results is the pulsed corona reactor. The industrial implementation of this reactor has the advantage of low retrofit cost since it can use the same wire-plate electrode arrangement as in electrostatic precipitators. Precipitators are commonly used for collecting particulate emissions in the utility, iron/steel, paper manufacturing, and cement and ore-processing industries. By driving the reactor with very short pulses of high voltage, short-lived discharge plasmas are created that consist of energetic electrons, which in turn produce the radicals responsible for the decomposition of the toxic molecules. Because of the short lifetime of the discharge, electrical power is not dissipated in the movement of ions, thus avoiding heating of the gas and providing good energy efficiency. Pulsed corona reactors have been shown, both in laboratory and industrial scale, to be very effective in the removal of many types of gaseous pollutants.

By driving the reactor with very short pulses of high voltage, short-lived discharge plasmas are created which consist of energetic electrons...

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In Japan, experiments done in 1981 at the University of Tokyo investigated the possibility of enhancing the pollutant removal efficiency of the electron-beam method by applying an electric field to regenerate energetic electrons in the plasma (Masuda et al. 1981). It was found that pulsed electric fields could be very effective when a corona discharge was created, even when the electron beam was switched off. Subsequent tests at Masuda Research were performed in an incineration plant to apply this technique to the removal of other pollutants such as mercury vapour (Masuda et al. 1987). Recently, experiments conducted by Ishikawajima Harima Heavy Industries Co. and Toyohashi University of Technology, applied the pulsed corona method to the removal of ethylene for fresh fruit and vegetable storage (Kamase et al. 1991). A study was recently commissioned by the Japanese Ministry of International Trade and Industry to perform technical and economic assessments of the pulsed corona process for utility boilers. The committee concluded that the method deserves development as the next generation technology for the removal of SO_2 and NO_x, and estimated its costs to be 25% lower than that of the best existing technology.

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Industrial-scale experiments on the use of pulsed corona for the simultaneous removal of NO_x and SO_2 from flue gas have been performed ... by the Italian National Electricity Board (ENEL) ... at the coal-burning power station in Marghera

Industrial-scale experiments on the use of pulsed corona for the simultaneous removal of NO and SO_2 from flue gas have been performed in Italy. The core of this project is a series of experiments carried out by the Italian National Electricity Board (ENEL), in collaboration with the University of Padova, at the coal-burning power station in Marghera near Venice (ENEL 1988) (Dinelli et al. 1990) . The ENEL tests have become the basis for the assessment of the electrical technology requirements of the pulsed corona process for applications to flue gas cleanup in actual power plants. The ENEL work has now evolved into a joint European Economic Community (EEC) project, with participation from Eindhoven University of Technology in the Netherlands and AEA Technology in the UK.

In the USA, laboratory experiments were conducted at Florida State University since 1983 that demonstrated the simultaneous removal of SO_2, NO_x and fly ash from effluent gases using the pulsed corona method

In the USA, laboratory experiments... demonstrated the simultaneous removal of SO_2, NO_x and fly ash from effluent gases using the pulsed corona method ... ... destruction of volatile organic compounds ... decomposition of hydrogen sulfide ...

(Clements et al. 1989). This work was supported in part by the US Department of Energy. The Research Triangle Institute has applied the pulsed corona method to the destruction of volatile organic compounds (Yamamoto et al. 1992). This program was started in 1988 under a US Environmental Protection Agency cooperative agreement and has also been supported by the US Navy. Complete destruction was obtained for toluene, and high conversions were achieved for methylene chloride and trichlorotrifluoroethane (CFC-113). Research-Cottrell has applied the pulsed corona method to the decomposition of hydrogen sulfide (H_2S) (Helfritch 1991). H_2S is a toxic by-product of several industrial processes, including petroleum refining, dyeing, synthetic rubber, viscose rayon, and leather-treating operations. Researchers at Lawrence Livermore National Laboratory have been conducting experiments on the use of pulsed-power-driven plasma devices to reduce the relative concentrations of nitrogen oxides and volatile organic compounds from various types of industrial processes.

Silent Discharge

In silent discharge reactors, AC high voltages are applied between electrodes, one or both of which are

Silent discharge processing is a very mature technology, first investigated by Siemens in the 1850's for the production of ozone ... for applications such as water purification ...

covered with a thin dielectric layer, such as glass. Silent discharges are also referred to as dielectric barrier discharges. The geometry is commonly either planar (parallel plates) or cylindrical (coaxial tubes). Configurations like those used in corona discharges are also used in which one of the electrodes (e.g. a wire) is highly stressed, and the outer electrode is a metal foil wrapped around a glass tube. Silent discharge processing is a very mature technology, first investigated by Siemens in the 1850's for the production of ozone. It is now routinely used to produce very large quantities of ozone for applications such as water purification, and the bleaching of textile and pulp.

Whereas in the pulsed corona method the transient behavior of the plasma is controlled by the applied voltage pulse, the plasma that takes place in a silent discharge self-extinguishes when charge build-up on the dielectric layer reduces the local electric field. For some applications, this feature presents an advantage for the silent discharge approach since simpler electrical power supplies can be used. In some cases, however, the efficiency of the silent discharge reactor is improved significantly by applying high-repetition-rate voltage pulses in a manner similar to that in pulsed corona reactors.

At Southern Illinois University, the plasma-assisted oxidation of SO_2 to SO_3 has been investigated using a silent discharge (Dhali et al. 1991). SO_3 is a more desirable byproduct of flue gas as opposed to SO_2 because it can be dissolved in water easily and can be reacted with lime to form gypsum. At the University of Illinois, the use of silent discharge processing for the removal of SO_2 from flue gas by conversion to sulfuric acid has been investigated (Chang et al. 1991). At the University of New Hampshire, the removal of NO has been investigated using a wire-cylinder silent discharge

The use of a silent discharge reactor as a second stage burner for removing hazardous organic materials from mixed waste is being investigated ...

electrode configuration with a catalytic material, such as glass wool, packed in between the electrodes (McLarnon et al. 1991). The works at the Southern Illinois University, and the University of New Hampshire were funded by the US Department of Energy, while the work at the University of Illinois was funded in part by the US Environmental Protection Agency.

Silent discharge reactors have also been demonstrated to decompose many types of hydrocarbon, halocarbon, and organophosphorous compounds.

Mixed waste, containing both chemical hazards and radionuclides, are usually volume reduced through incineration and the residue packaged for long-term storage. The use of a silent discharge reactor as a second stage burner for removing hazardous organic materials from mixed waste is being investigated at Los Alamos National Laboratory (McCulla et al. 1991). Tests using a prepared gaseous feed containing trichloroethylene (TCE), carbon tetrachloride (CCl_4), n-octane and CFC-113 are encouraging.

The use of silent discharge processing for detoxifying chemical warfare gases has been investigated in several US laboratories. In 1985, work at the Naval Research Laboratory (NRL), funded by the US Office of Naval Research, demonstrated the decomposition of the simulant gas dimethyl-methyl-phosphate (DMMP) (Fraser et al. 1985). Collaborative work between Auburn University and the US Army Chemical Systems Laboratory demonstrated the decomposition of phosphonofluoride acid vapors (Clothiaux et al. 1984). Work at SRI International, with funding from the Wright-Patterson Air Force Base, studied the discharge-induced destruction of the simulants DMMP, DEMP, and O,S-DEMP (Slanger et al. 1990). The silent discharge-induced decomposition of methane, hydrogen cyanide, formaldehyde and benzene have also been reported in the experiments at NRL and Auburn (Fraser et al. 1985) (Fraser et al. 1986) (Neely et al. 1985) (Neely et al. 1988).

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The US Army Chemical Research, Development and Engineering Center - sponsored technical evaluation of plasma air purification technology has identified several areas for further work required to mature plasma reactors for potential military application.

The US Army Chemical Research, Development and Engineering Center (CRDEC) has recently conducted an evaluation of plasma technology for military air purification applications (Tevault 1992). Plasmas offer several advantages over the standard filtration approach, using activated impregnated carbon, in that all known military chemical and biological warfare agent can be decontaminated by passing through a plasma reactor. The CRDEC-sponsored technical evaluation of plasma air purification technology has identified several areas for further work required to mature plasma reactors for potential military application.

At the Kurchatov Institute of Atomic Energy in Russia, the use of short high-voltage pulses is applied to dielectric-barrier reactors to increase the efficiency for the removal of dilute amounts of H_2S, CS_2, SO_2 and mercoptans in various gas mixtures. A pilot plant is being constructed to demonstrate the use of this technology for air purification in the paper industry.

In Japan, collaborative work between Ibaraki University and Niles Parts Co. has resulted in the development of a near-practical plasma reactor that can simultaneously remove NO_x, SO_x, CO_x and soot from diesel engine exhaust (Higashi et al. 1992). This work began in 1979 following the failure of an effort to develop an exhaust gas recirculation (EGR) system to reduce NO_x emission from diesel engines. Although the primary goal was achieved, the recirculation of soot-laden gases led to decreased engine power and increased the wear on the valves, valve seats, piston surfaces and cylinder walls. In their cylindrical plasma reactors, the inner electrode was a stainless metal screw and the outer electrode was aluminum foil wrapped around a glass tube. The reactor was energized by AC high voltage. The major innovation in their work was the addition of drops of oil into the gas stream that were transformed into a dielectric mist. This produced a more homogeneous discharge and led to the complete elimination of soot, as well as the removal of NO_x, SO_x and CO_x.

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Surface Discharge

The use of surface discharge processing for the destruction of gaseous pollutants has been demonstrated in collaborative work between Masuda Research, University of Tokyo and Takuma Co (Masuda et al. 1985). The reactor consists of a planar or cylindrical alumina ceramic having a series of strip-like electrodes attached on one of its surface and a film-like counter electrode embedded inside the ceramic. A high-

The surface discharge reactor has been applied to the removal of NO_x in the combustion gas from an oil-burning boiler and the exhaust from a diesel engine... It has also been demonstrated that freons ... can be destroyed without the production of poisonous by-products

frequency AC high-voltage is applied to generate the surface discharge, starting from the side edges of the strip electrodes and uniformly covering the ceramic surface.

The surface discharge reactor has been applied to the removal of NO_x in the combustion gas from an oil-burning boiler and the exhaust from a diesel engine (Masuda et al. 1991). It has also been demonstrated that freons such as CFC-22 and CFC-113 can be destroyed without the production of poisonous by-products such as phosgene (Oda et al. 1991).

Ferroelectric Bed

The ferroelectric bed reactor employs a high-voltage AC power supply in conjunction with a tubular reactor packed with high-dielectric ceramic pellets. The pellets are held within the tube arrangement by two metal mesh electrodes. When external AC voltage is applied across the high dielectric layer, the pellets are polarized, and an intense electric field is formed around each pellet contact point. Many pulsed discharges take place around each contact point of the ferroelectric pellets, and the discharge energy can be controlled by changing the dielectric constant of the pellet, and by the voltage waveform.

At Toyohashi University of Technology in Japan,

... experiments have been carried out on the reduction of carbon dioxide ... the ferroelectric bed can destroy a variety of hazardous organic compounds

the ferroelectric bed reactor has been used to decompose methane diluted in various gas mixtures (Mizuno et al. 1988). In a joint work with McMaster University in Canada, experiments have been carried out on the reduction of carbon dioxide (Jogan et al. 1991). In the USA, experiments by Research Triangle Institute and the US Environmental Protection Agency have demonstrated that the ferroelectric bed can destroy a variety of hazardous organic compounds, including toluene, methylene chloride and CFC-113 (Yamamoto et al. 1992).

Microwave Discharge

The potential for using microwave discharges to destroy toxic molecules was demonstrated at the Lockheed Palo Alto Research Laboratory, in collaboration with Edgewood Arsenal, University of California at Berkeley, and the US Environmental Protection Agency (Bailin et al. 1975) (Bailin et al. 1978). Using microwave plasmas at sub-atmospheric pressures, they were able to destroy a wide range of hazardous mol-

The potential for using microwave discharges to destroy toxic molecules was demonstrated... able to destroy a wide range of hazardous molecules ...

ecules, including chlorinated hydrocarbons such as PCB's and organophosphorous compounds such as malathion. They also showed that metallic mercury can be recovered from the decomposition of phenylmercuric acetate (PMA), and performed an interesting series of experiments on the simulants DIMP and DMMP.

Experiments at the Kurchatov Institute in Russia (Bagautdinov et al.) and at Argonne National Laboratory in the USA (Harkness et al.) have demonstrated the use of microwave discharges for dissociating hydrogen sulfide. The plasma process has the advantage of being able to recover hydrogen, as well as sulfur, from the hydrogen sulfide.

Microwave systems for producing large volumes of non-thermal plasma in atmospheric-pressure gases have been proposed by investigators at AMPC Inc. (Guest et al. 1989) and the Naval Surface Weapons Center (Uhm et al. 1991).

Discharge in Fast Gas Flow

A discharge can be established using a simple DC

The use of fast gas flow for the stabilization of a point-to-plane corona discharge ... detoxification of chemical warfare gases...

high-voltage power supply. The construction of the reactor is simple, typically consisting of an anode plate and a cathode containing a lot of sharp metallic pins. By pumping the gas through the discharge volume to produce fast flow at atmospheric or superatmospheric pressure (1 - 2 atm), a stationary discharge can be established without overheating the gas. The use of fast gas flow for the stabilization of a point-to-plane corona discharge has been investigated by Westinghouse Corporation in the USA (Castle et al. 1984). The Research Triangle Institute has applied a similar technique to the detoxification of chemical warfare gases (Yamamoto et al. 1988) (Yamamoto et al. 1989). Researchers at the Troitsk Institute in Russia report to have improved the implementation of this type of reactor and achieved very good efficiencies in the oxidation of pollutant molecules (Akishev et al. 1991). They used flow speeds of up to 200 m/s across the discharge. In France, researchers at the University of Orleans have developed a technique using tapered gaps, called a gliding discharge, in which the stationary glow discharge is replaced by a moving arc (Czernichowski et al. 1991). This operates at much lower gas flow speeds of around 10 m/s. The results obtained with a variety of pollutants, such as hydrogen sulfide, methyl mercaptan and tetrachloroethylene, are very encouraging.

a technique using tapered gaps, called a gliding discharge ... results obtained with a variety of pollutants ... are very encouraging

Another device, the corona torch, was developed to enlarge the active volume of the corona discharge. The gas flow enters an upstream cylindrical hollow electrode and exits at a downstream cylindrical hollow electrode. All the reactive gas pass through the active plasma zone. High-speed gas flow near the exit of the electrode cool the electrodes; hence, the chemical reactions and the stability of the discharge is enhanced. This device has been applied to the removal of CO_2 in combustion gases (Maezono et al. 1990).

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Pollution Control Workshop

Non-thermal plasma techniques offer several new cost-effective technologies that could dispose of many types of gaseous pollutants, sometimes even simultaneously. This field has grown dramatically in recent years. Many new types of air pollutants have been tackled; new kinds of plasma reactors have been developed, and existing kinds have been improved greatly. It is in the interest of many nations to assure that all practical and economically feasible steps are taken to apply and further develop these techniques to help solve the preeminent environmental problems of acid rain, global warming, ozone depletion, and smog. To accomplish this, it is necessary to get the best solutions from industry, academia, and government laboratories, and to pool this information for the benefit of all. The "NATO Workshop on Non-Thermal Plasma Techniques for Pollution Control" to be held in Cambridge University on Sept. 21-25, 1992, was conceived as a step towards that goal.

It is in the interest of many nations to assure that all practical and economically feasible steps are taken to apply and further develop these technqiues to help solve the preeminent environmental problems of acid rain, global warming, ozone depletion, and smog.

The workshop is sponsored by the NATO Scientific and Environmental Affairs Division, the US Army European Research Office, and the US Office of Naval Research European Office. The industrial sponsors include Asea Brown Boveri, Ebara Corporation (Japan), Asahi Kogyosha Co. Ltd. (Japan), NV KEMA (The Netherlands), Maxwell Laboratories (USA), Ansaldo (Italy) and Officine Galileo (Italy).

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SCHEDULE

INTRODUCTION

0900 - 0915	**Introductory Remarks**
0915 - 0945	**Overview of Atmospheric Pollution Problems** R. Derwent Department of Environment - (UK)
0945 - 1005	**The Need for Mixed Waste Treatment Options Within the US Department of Energy** W. H. McCulla Los Alamos National Laboratory - (USA)
1005 - 1035	**The History of Electron Beam Processing for Environmental Pollution Control and Work Performed in the United States** N. W. Frank and S. Hirano Ebara Environmental Corporation - (USA)
1035 - 1050	BREAK
1050 - 1120	**Energetic Electron Induced Plasma Processes for Reduction of Acid and Greenhouse Gases in Combustion Flue Gas** J.-S. Chang McMaster University - (Canada)
1120 - 1140	**High Pressure Discharge as a Trigger for Pollution Control** E. Marode, A. Goldman, and M. Goldman Ecole Supérieure d' Electricité - (France)
1140 - 1230	DISCUSSION Topic: Problem Definition - Goals of the Workshop - Overview of Alternative Techniques - Who Pays for It?
1230 - 1330	LUNCH
1330 - 1430	POSTERS - SET 1 (To be displayed all day on Monday and Tuesday)

APPLICATIONS

MILITARY APPLICATIONS

1430 - 1500 **Application of Plasma Technology for Military Air Purification Applications**
D. E. Tevault
U. S. Army CRDEC - (USA)

APPLICATION TO MOBILE SOURCES

1500 - 1530 **Simultaneous Removal of NO_x, CO_x, SO_x and Soot in Diesel Engine Exhaust**
K. Fujii, M. Higashi*, and N. Suzuki*
Ibaraki University - (Japan)
*Niles Parts Co. Ltd. - (Japan)

INDUSTRIAL-SCALE TESTS OF FLUE GAS TREATMENT

1530 - 1600 **Application of E-Beam Treatment to Flue Gas Cleanup in Japan**
A. Maezawa and M. Izutsu
Ebara Corporation - (Japan)

1600 - 1630 **Industrial Application of Pulsed Corona Processing to Flue Gas**
L. Civitano
ENEL - (Italy)

1630 - 1645 BREAK

1645 - 1800 DISCUSSION
Topic: Overview of Non-Thermal Plasma Techniques
- Approaches to be Discusssed
- Targets
- Critical Issues

1900 - 2100 DINNER

ELECTRON BEAM PROCESSING

APPLICATION TO FLUE GAS TREATMENT

0900 - 0920 **Chemical Kinetics Model of SO_2/NO_x Removal by Electron Beam**
H. Mätzing
Kernforschungszentrum Karlsruhe GmbH - (Germany)

0920 - 0940 **Experiments on Chemical Reaction in Electron-Beam-Induced NO_x/SO_2 Removal**
O. Tokunaga and H. Namba
Japan Atomic Energy Research Institute - (Japan)

0940 - 1000 **SO_2 and NO_x Removal from Flue Gas by Means of Lime Spray Dryer Followed by Electron Beam Irradiation**
D. J. Helfritch
Research-Cottrell Inc.- (USA)

1000 - 1020 **Investigation of SO_2 Oxidation in Humid Air Stream by High Current Density Pulsed Electron Beam**
E. I. Baranchicov, G. S. Belenky, M. A. Deminsky, V. P. Denisenko, D. D. Maslenicov, B. V. Potapkin, V. D. Rusanov, A. M. Spector, E. V. Shulakova, and A. A. Fridman
Kurchatov Institute of Atomic Energy - (Russia)

1020 - 1035 BREAK

1035 - 1055 **Electron Beam Flue Gas Treatment in Poland**
A. G. Chmielewski and Z. Zimek
Institute of Nuclear Chemistry and Technology - (Poland)

APPLICATION TO COMPLEX MOLECULES

1055 - 1115 **Removal of Volatile Hydrocarbons from Industrial Off-Gas**
H.-R. Paur
Kernforschungszentrum Karlsruhe GmbH - (Germany)

1115 - 1135 **UV and Electron Beam Degradation of Chlorinated Hydrocarbons and Aromatics**
H. Esrom, H. Scheytt*, R. Mehnert**, and C. v. Sonntag***
Asea Brown Boveri AG - (Germany)
*Asea Brown Boveri AG - (Germany) and Universität Karlsruhe - (Germany)
** Instiut für Oberflächenmodifizierung e. V. - (Germany)

***Max-Planck-Institut für Strahlenchemie - (Germany)

1135 - 1230 **DISCUSSION**

Topic: Status of Electron Beam Technology

- Unsolved Scientific & Technical Problems
- Conclusions from Past Tests & Economic Analyses
- Unresolved Commercial Issues

1230 - 1330 LUNCH

1330 - 1430 **POSTERS - SET 1**

(To be displayed all day on Monday and Tuesday)

DC DISCHARGE PROCESSING

1430 - 1450 **Gliding Discharge Reactor for H_2S Valorization or Destruction**
A. Czernichowski
Université d'Orléans - (France)
H. Lesueur
Bureau de Recherches Géologiques et Minières - (France)

1450 - 1510 **DC Glow Discharge with Fast Gas Flow for Flue Gas Processing**
A. P. Napartovich
Troitsk Kurchatov Research Institute - (Russia)

1510 - 1530 **Decomposition of NO_2 by Glow Discharge Plasma**
Y. Sakai and H. Tagashira
Hokkaido University - (Japan)

1530 - 1550 **Negative Corona-Induced Decomposition of CCl_2F_2**
J. D. Skalny, V. Sobek, and P. Lukác
Comenius University - (Czechoslovakia)

SILENT DISCHARGE PROCESSING

APPLICATION TO GREENHOUSE GASES

1550 - 1610 **Hydrogenation of CO_2 in a Silent Discharge**
B. Eliasson, F. Simon, and W. Egli
Asea Brown Boveri - (Switzerland)

APPLICATION TO UV PRODUCTION

1610 - 1630 **UV Production in Dielectric-Barrier Discharges for Pollution Control**
U. Kogelschatz
Asea Brown Boveri - (Switzerland)

1630 - 1645 BREAK

1645 - 1800 DISCUSSION
Topic: Discharge Approaches to Gas Cleaning
- Types of Plasma Discharge
- Characteristics of Effective Discharges
- Unresolved Scientific and Technical Problems

1900 - 2100 SPECIAL DINNER

SILENT DISCHARGE PROCESSING

BASIC DISCHARGE MECHANISMS

0900 - 0920 **Modelling of Dielectric Barrier Discharges**

G. J. Pietsch, D. Braun*, and V. I. Gibalov#
Aachen University of Technology - (Germany)
*now with Hartmann & Braun AG - (Germany)
#Moscow State University - (Russia)

APPLICATION TO COMPLEX MOLECULES

0920 - 0940 **Decomposition of Complex Molecules Using Silent Discharge Processing**

W. C. Neely, E. I. Newhouse, E. J. Clothiaux, and C. A. Gross
Auburn University - (USA)

0940 - 1000 **Treatment of Hazardous Organic Wastes Using Silent Discharge Plasmas**

L. A. Rosocha, G. K. Anderson, L. A. Bechtold, J. J. Coogan, H. G. Heck, M. Kang, W. H. McCulla, R. A. Tennant, and P. J. Wantuck
Los Alamos National Laboratory - (USA)

1000 - 1020 **Removal of Organophosphonate Chemical Agents from Air Streams**

T. G. Slanger and R. L. Sharpless
SRI International - (USA)

1020 - 1035 BREAK

AC DISCHARGE PROCESSING

1035 - 1105 **Destruction of Gaseous Pollutants and Air Tocixs by Surface Induced Plasma Chemical Process (SPCP) and Pulse Corona Induced Plasma Chemical Process (PPCP)**

S. Masuda
Fukui University of Technology - (Japan)

to be presented by

K. Sakakibara
Takuma Co. Ltd. - (Japan)

1105 - 1135 **Application of Corona Technology to the Reduction of Greenhouse Gases and Other Gaseous Pollutants**

A. Mizuno, A. Chakrabarti, and K. Okazaki
Toyohashi University of Technology - (Japan)
to be presented by
Y. Matsumoto
Asahi Kogyosha Co. Ltd. - (Japan)

1135 - 1205 **Decomposition of Volatile Organic Compounds by a Packed Bed Reactor and a Pulsed Corona Plasma Reactor**
T. Yamamoto, P. A Lawless, M. K. Owen, and D. S. Ensor
Research Triangle Institute - (USA)
C. Boss
North Carolina State University - (USA)

1205 - 1230 QUESTION & ANSWER PERIOD

1230 - 1330 LUNCH

1330 - 1430 POSTERS - SET 2
(To be displayed all day on Wednesday and Thursday)

AC DISCHARGE PROCESSING (continued)

1430 - 1450 **Reaction Kinetics for Flue Gas Treatment of NO_x**

R. W. Breault and C. McLarnon
Tecogen, Inc. - (USA)
V. K. Mathur
University of New Hampshire - (USA)
M. Landau
SoCal Gas Company

PULSED CORONA PROCESSING

APPLICATION TO FLUE GAS TREATMENT

1450 - 1510 **Modeling of Plasma Catalytic Reduction of NO_x and SO_2 in Flue Gases**

I. Gallimberti
University of Padova- (Italy)
to be presented by
M. Rea
University of Padova - (Italy)

1510 - 1530 **Experimental Studies on NO Removal Using Streamer Corona**

R. H. Amirov, E. I. Asinovsky, I. S. Samoilov, and
A. V. Shepelin
Institute for High Temperatures - (Russia)

1530 - 1550 **Pulsed Coronal Discharge for Combined Removal of SO_2, NO_x and Fly Ash From Flue Gas**

G. E. Vogtlin
Lawrence Livermore National Laboratory - (USA)
to be presented by
J. N. Bardsley
Lawrence Livermore National Laboratory - (USA)

APPLICATION TO OTHER GASEOUS POLLUTANTS

1550 - 1610 **Hydrogen Sulfide Decomposition by Means of Pulsed Corona Discharge**

D. J. Helfritch
Research-Cottrell Inc. - (USA)

1610 - 1630 **Laboratory Studies of Plasmochemical Oxidation Process Energized by Pulsed Streamer Discharges**

V. A. Abolentsev, S. V. Korobtsev, D. D. Medvedev,
V. D. Rusanov, and **V. L. Shiryaevsky**

Kurchatov Institute of Atomic Energy - (Russia)

1630 - 1645 BREAK

1645 - 1800 DISCUSSION

Topic: Plasma Morphology and Physics

- Comparison of Different Discharge Techniques
- Effiency & Uniformity
- Lifetime & Industrial Compatibility

1900 - 2100 DINNER

FUNDAMENTALS

DIAGNOSTICS OF CORONA DISCHARGE PROCESSES

0900 - 0920 **Emission Spectroscopy of Corona Discharges**
T. H. Teich
Swiss Federal Institute of Technology - (Switzerland)

0920 - 0940 **Electrical and Optical Investigation of Pulsed Streamer Corona**
Y. Creyghton, E. M. van Veldhuizen, and W. R. Rutgers
Eindhoven University of Technology - (The Netherlands)

MODELING OF CORONA DISCHARGE PROCESSES

0940 - 1000 **Theory of Pulsed Corona in Air and Flue-Gas Mixtures**
R. Morrow
CSIRO Division of Applied Physics - (Australia)

1000 - 1020 **Multi-Dimensional Modeling of the Dynamic Morphology of Streamer Coronas**
P. A. Vitello, B. M. Penetrante, and J. N. Bardsley
Lawrence Livermore National Laboratory - (USA)

1020 - 1035 BREAK

COLLISION PROCESSES

1035 - 1055 **The Role of Electron Attachment to Gas Molecules in Electrostatic Precipitators**
J. J. Lowke
CSIRO Division of Applied Physics - (Australia)

1055 - 1115 **Electron Data Base Needed For Discharge Modeling in Flue Gas Treatment**
M. Yousfi, A. Poinsignon, and A. Hamani
Université Paul Sabatier - (France)

1115 - 1135 **Swarm Determination of Electron-Molecule Cross-Sections in Some Hydrocarbon Gases such as Methane, Propane and Isobutane**
P. Ségur and M. C. Bordage
Université Paul Sabatier - (France)

1135 - 1230 DISCUSSION
Topic: Plasma Physics Issues
- How Good is Our Scientific Base?

- Collisional Cross Sections and Reaction Rates
- Diagnostics

1230 - 1330 LUNCH

1330 - 1430 **POSTERS - SET 2**
(To be displayed all day on Wednesday and Thursday)

CHEMICAL KINETICS

1430 - 1450 **Influence of Active Radicals on NO/SO_2 Removal from Flue Gases in Corona Discharge Installations**

G. Alekseev, A. Levchenko, F. van der Vleuten* and V. Bityurin
Institute for High Temperatures - (Russia)
*Eindhoven Univ. of Technology - (The Netherlands)

1450 - 1510 **The Effect of Clusters and Heterogeneous Reactions on Non-Equilibrium Plasma Flue Gas Cleaning**

A. A. Fridman, B. V. Potapkin, and V. D. Rusanov
Kurchatov Institute of Atomic Energy - (Russia)

1510 - 1530 **Chemical Kinetic Data for Modeling Non-Thermal Plasmas**

J. T. Herron
National Institute of Standards and Technology - (USA)

1530 - 1630 DISCUSSION

Topic: Plasma Chemistry Issues

- Unresolved Chemistry Issues
- Undesirable By-Products
- Coupling between Chemistry and Plasma Morphology

1630 - 1645 BREAK

1645 - 1800 ROUND TABLE DISCUSSION

Topic: Industrial Perspective

- Assessment of Past Work
- Issues of Commercial Implementation
- Priorities for Further Work
- Economic Analyses

1900 - 2100 DINNER

TECHNOLOGY DEVELOPMENTS

0900 - 0920 **Plasma Arc Processing of Solid and Liquid Wastes**
M. P. Schlienger
Retech, Inc. - (USA)

0920 - 0940 **Energization of Pulse Corona Induced Chemical Processes**
M. Rea, K. Yan*, and L. Sonaglioni
University of Padova - (Italy)
*Beijing Institute of Technology - (China)

0940 - 1000 **Design and Initial Testing Results from the Repetitive High Energy Pulsed Power (RHEPP) Project**
E. L. Neau, H. C. Harjes, K. W. Reed, K. J. Penn, R. W. Wavrik, D. L. Johnson, C. R. McClenahan, and K. R. Prestwich
Sandia National Laboratories - (USA)

1000 - 1020 **High Average Power Modulator and Accelerator Technology Developments at Physics International**
P. Sincerney, S. Ashby, J. Benford, C. Deeney, G. Frazier, J. Levine, J. Meachum, and L. Schlitt*
Physics International Company - (USA)
*Consulting Services, Livermore, CA - (USA)

1020 - 1035 BREAK

1035 - 1055 **Development of the Electron Beam Dry Scrubbing of Flue Gas Utilizing High Power Transformer (HPTA) Technology**
R. D. Genuario, S. Eckhouse, and J. Ratifia-Brown
Science Applications International Corporation - (USA)

1055 - 1125 **Participation of the Institute of Nuclear Physics (Novosibirsk) in Programs of Electron Beam Flue Gas Treatment and Development of High Power Accelerators**
R. A. Salimov
Institute of Nuclear Physics, Novosibirsk - (Russia)
Ansaldo - (Italy)

1125 - 1145 **Research to Improve the Efficiency of Pulsed Power Switches and Beams for High Average Power Systems for Pollution Control**
M. A. Gundersen, T. Y. Hsu, and R. L. Liou
University of Southern California - (USA)

1145 - 1205 **A Long Life, High Repetition Rate Electron Beam Source**
S. J. Scott
The Sowerby Research Centre - (UK)

1205 - 1225 **Generation of Electron Beam for Technological Processes**
S. Pekárek and J. Rosenkranz
Czech Technical University - (Czechoslovakia)

1230 - 1330 LUNCH

1330 - 1530 DISCUSSION

Topic 1: Critical Technologies
- Best Available Technologies for Pollution Control Using Electron Beam and Discharge Techniques
- Urgently Needed Improvements

Topic 2: Recommendations for Further Research
- Priorities for Basic and Applied Research
- Opportunities for International Collaboration

1900 - 2100 DINNER

INTRODUCTION

THE NEED FOR MIXED WASTE TREATMENT OPTIONS WITHIN THE US DEPARTMENT OF ENERGY*

William H. McCulla
Los Alamos National Laboratory
Los Alamos, New Mexico 87545 USA

The United States Department of Energy is in the process of beginning a clean-up of many of its facilities of waste containing radioactive and hazardous components (mixed waste). Many of these waste streams had been previously disposed of by methods acceptable at the time but with the passage of very stringent laws effecting migration of hazardous components now the disposal areas constitute remediation sites. Disposal of low level radioactive waste potentially containing hazardous materials have also fallen under land disposal restrictions and currently no mixed waste is going to low level disposal facilities. Conventional methods of destroying the hazardous components have often either been difficult to implement because of the radioactive component or have met considerable opposition from the governmental or public sectors Most of the opposition centers on concerns on pollution of the environment by either or both the radioactive and hazardous components. Innovative technical solutions for waste disposal that address public concerns on pollution are needed in as short a time as possible to unlock the log jam of out-of-regulatory-compliance stored mixed waste.

With this background of few acceptable methods for mixed waste disposal and a driving need to find acceptable solutions the DOE has embarked on a national mixed waste program to develop solutions to the waste disposal problem. A systems approach of looking at all necessary steps to convert a waste stream as it presently exist to a final form acceptable for disposal is being undertaken. Baseline technologies for each step are analyzed for acceptability and potentially better or more innovative technology candidates are compared to the baseline. Technologies that compare favorably to the baseline offer options for more effective destruction of the hazardous components, reduced or eliminated secondary hazardous waste generation, and/or offer a solution that may be more acceptable and easily permittable. This program is developing a close working relationship with the Environmental Protection Agency (EPA), the U.S. national regulatory agency for the environment, and where possible the effected state regulatory agencies to improve their understanding of the DOE's needs and to help expedite the permitting process.

Plasma technologies have already begun to play important roles as potentially more effective methods for organic waste destruction in environmental remediation and waste treatment. Several plasma technologies are being planned or have been successfully tested at a contaminated spill site where trichloroethylene (TCE) is being pumped from the ground and the plasma systems destroy the TCE in air before it is released to the environment. This has significant advantages over conventional approaches such as carbon absorption which is fairly expensive, tends to degrade rapidly due to non-selective absorption, and presents a secondary waste that requires destruction. Similar technologies such as in situ corona discharge will be or have been applied to carbon tetrachloride spills at another DOE site.

Hot plasma systems are being considered for primary destruction of combustible and hazardous constituent contaminated waste. This process has the potential advantage of removing the organic hazardous components, volume reduction and encapsulation of the noncombustible components in a glass matrix. Cold plasma technologies are being tested as potentially more versatile if not more effective secondary units for replacement of conventional thermal treatment units. Conventional thermal treatment has the disadvantages of creating NO_X problems, greatly increasing the volume flow through the system making scrubbing and particulate removal more difficult, and generally not responding well to upset conditions unless substantially oversized for normal operations. Plasma systems have shown advantages such as rapidly adjusting power loads to meet large swings in pollutant concentrations, removing pollutants without increasing gas volume flow, and generally less susceptibility to corrosion due to lower temperature of operation.

Plasma technology has already begun to make some significant inroads in waste destruction and pollution abatement, particularly within the Department of Energy Complex. But it still does not enjoy the kind at confidence that conventional thermal technologies enjoy. We can hope that as the plasma technology matures and we are able to show not only significant technical and economic advantages but also reliability that plasmas will become the methods of choice for waste destruction and pollution control.

*This work was performed at Los Alamos National Laboratory under the auspices of the United States Department of Energy under contract number W-7405-ENG-36.

THE HISTORY OF ELECTRON BEAM PROCESSING FOR ENVIRONMENTAL POLLUTION CONTROL AND WORK PERFORMED IN THE UNITED STATES

Norman W. Frank and Shinichi Hirano
Ebara Environmental Corporation
Hempfield Industrial Park
R.D. #6, Box 516
Greensburg, Pennsylvania 15601 USA

The Electron Beam Process is a dry-scrubbing process which simultaneously removes sulfur dioxide (SO_2) and nitrous oxides (NO_x) from combustion flue gases. The irradiation of the flue gas produces active radicals and atoms which react with the SO_2 and NO_x to form their respective acids. In the presence of ammonia (NH_3), these acids are converted to ammonium sulfate $(NH_4)_2SO_4$ and ammonia sulfate-nitrate $(NH_4)_2SO_4$-$2NH_4NO_3$. Other organic compounds can also be treated using the same principles.

The process is simple and as an example, in a utility power plant the gas would be partially cleaned of flyash by a particle collector. It then passes through an evaporative spray cooler where the gas temperature is lowered as the humidity is increased. The gas then passes to the E-beam process vessel where it is irradiated by a beam of high-energy electrons in the presence of a near-stoichiometric amount of ammonia which has been added to the flue gas upstream of the vessel. Oxidation of the SO_2 and NO_x occurs to form products which subsequently react with the added ammonia to form ammonium sulfate and ammonium sulfate-nitrate. These salts are recovered as a dry powder using a conventional particle collector. The collected powder is potentially salable as an agricultural fertilizer.

Research into radiation of flue gas was initiated by the Ebara Corporation, Japan, in 1970. These studies were to define the radiation-chemical reactions of SO_2 and NO_x resulting from the irradiation of flue gases. The success of these initial batch tests indicated excellent potential for the Electron Beam process. Subsequent development of the process was the result of a joint effort by Ebara and the Japan Atomic Energy Research Institute (JAERI) in 1972. After this joint effort, Ebara was encouraged to build a 1,000 Nm^3/h heavy-oil combustion gas pilot plant in 1974 to demonstrate the scale-up principles of the Electron Beam process.

In 1977, Ebara, in a joint effort with Nippon Steel and others, built and tested a 10,000 Nm^3/h Flue Gas Treatment Demonstration Plant to remove SO_2 and NO_x from the exhaust gas of a steel sintering plant.

In 1983, Ebara International Corporation (Predecessor Company to Ebara Environmental Corporation), under a cost sharing agreement with DOE, embarked upon a program to build and operate the Process Development Unit at Indianapolis Power and Light Company's E. W. Stout plant near Indianapolis, Indiana in order to evaluate this process on a coal-fired utility boiler flue gas.

In 1984, Research Cotrell conducted tests under a contract from the Department of Energy to study the effects of an alternate reagent on the Electron Beam process. In 1984, the Nuclear Research Center in Karlsruhe Germany and the University of Karlsruhe built pilot scale plants to study the reaction mechanisms of the process. In 1984, Badenwerk utility built a 180 kilowatt, 20,000 Nm^3/h Electron Beam pilot plant. Since the 500 megawatt boiler already had a conventional limestone SO_2 scrubbing process, the testing addressed NO_x removal.

In 1990, the Nuclear Research Center in Karlsruhe added a second pilot facility to continue work on mechanisms and filtration. Simultaneously in 1989, the Institute of Nuclear Chemistry and Technology in Warsaw, Poland built a small laboratory test unit for this process and began planning a 20,000 Nm^3/h demonstration facility. Both facilities are operational as of this date. In 1991, Ebara Corporation built a 1,000 Nm^3/h test facility at the Fujisawa Research Institute to make further studies to reduce capital and operating costs.

In 1992, a 12,000 Nm^3/h coal burning facility will be completed in Nagoya Japan at Chubu Electric Company. This facility will operate on various imported coals to demonstrate the process with a wide variety of fuels. Testing will be done with two (2) and three (3) zones of irradiation to reduce the operating costs of the process and improve NO_x removal efficiencies at lower power input.

Also in 1992, a plant to treat ventilation gases from automobile tunnels will be operational to reduce the amount of NO_x and unburned hydrocarbons from entering the atmosphere. This plant has a capacity of 50,000 Nm^3/h.

Highlights of each of the research efforts will be presented with emphasis on certain factors which were important for the next steps.

In addition, an in-depth analysis of the U.S. efforts will be discussed.

ENERGETIC ELECTRON INDUCED PLASMA PROCESSES FOR REDUCTION OF ACID AND GREENHOUSE GASES IN COMBUSTION FLUE GAS

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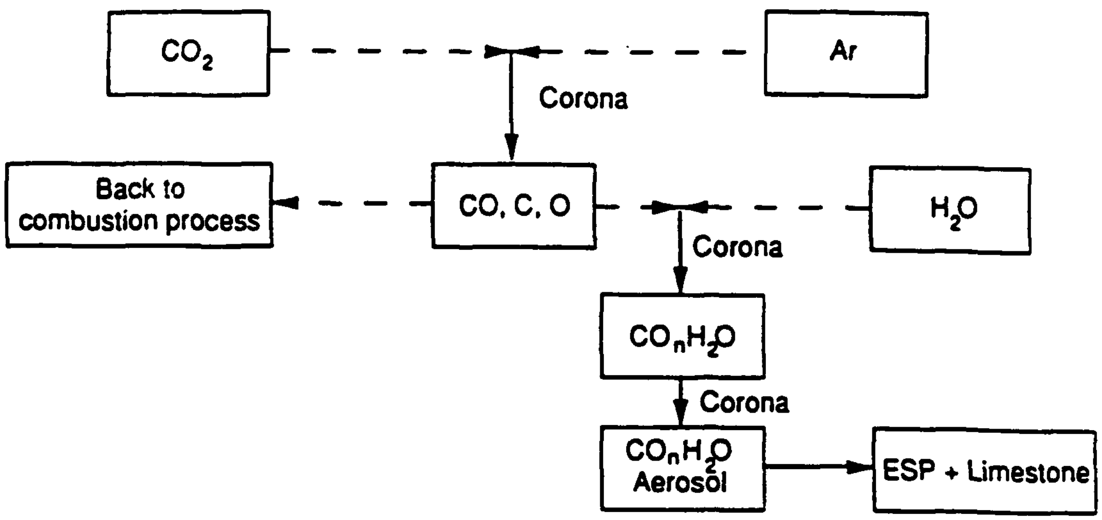
In gas cleaning of combustion flue gases, normally three approaches are proposed as follows:

1. Conversion of acid and greenhouse gases to harmless gases such as H_2O, N_2, O_2, etc.
2. Conversion of acid and greenhouse gases to reusable products such as salable agricultural fertilizers, dry ice, etc.
3. Trapping reformed acid and greenhouse gas byproducts such as ammonium sulfate aerosols, ammonium sulfate nitrate aerosols, carboxylic acid aerosols, carbon dust, etc.

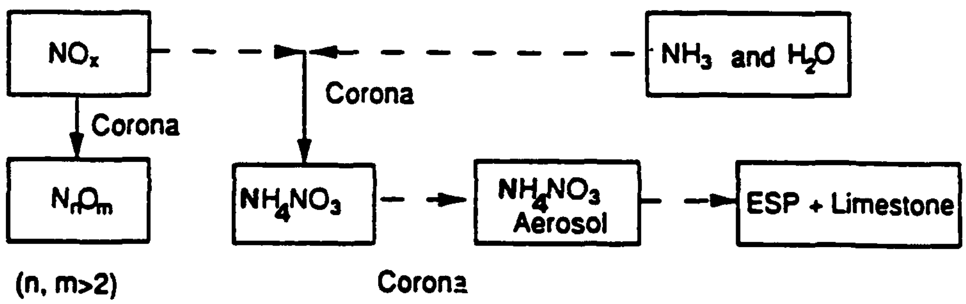
The energetic electron induced plasma process is one of the most effective methods of reducing SO_2, NO_x and CO_2 from industrial flue gases. This flue gas treatment consists of adding a small amount of ammonia, water vapour and/or argon gases, and irradiating the gas by means of an electron shower generated by an electron beam or corona discharge, thereby causing reactions which convert the acid and greenhouse gases to harmless gases, aerosols and other products. These products may then be collected from the flue gas by means of conventional collectors such as an electrostatic precipitator or baghouse [1]. In this paper, mechanisms of electron induced plasma processes for acid and greenhouse gas cleaning in a combustion flue gas are proposed. Detailed discussion will be presented for electron initiated molecule dissociations, ion-molecule reaction induced processes, radical chemistries for molecular gas conversions, and gas phase to particle conversion processes. Based on the proposed mechanisms, a critical review and recommendations are given for a reactor design, particle collection systems and energy efficient flue gas temperature control systems.

[1] J. S. Chang, P. A. Lawless, and T. Yamamoto, "Corona Discharge Processes", *IEEE Trans. Plasma Science* 19, 1152-1166 (1991).

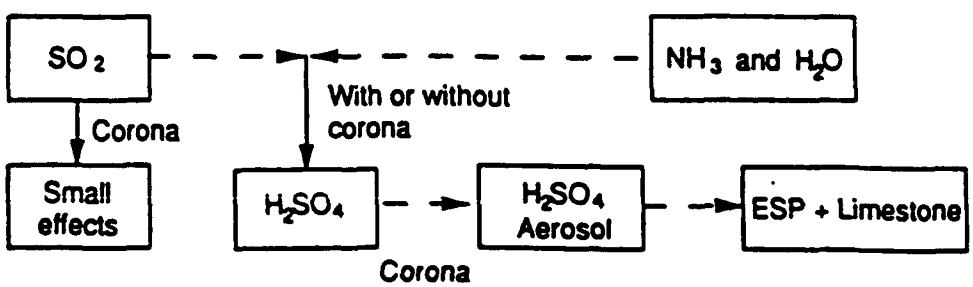
(a) CO_2 Reduction Process



(b) NO_x Oxidation Process



(c) SO_x Oxidation Process



HIGH PRESSURE DISCHARGE AS A TRIGGER FOR POLLUTION CONTROL

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High pressure plasma sources are nowadays often based on corona discharge, a classical way to build non-thermal plasma reactors.

Obviously. high pressure discharges may be induced by different kinds of electrical generators, ranging from DC to microwave generators, and various gap arrangements, including dielectric barriers. But if the frequency of the electrical generator remains under the RF range, including DC, the most common type of discharge invoked to be the basis of the generated plasma is corona discharge or corona triggered spark discharges. This paper discusses some aspects of the corona concept mainly under the DC case which gives a basic image of the various corona mechanisms.

The difficulty is that a large number of different discharge regimes, and discharge sequences, are put under the general label of Corona discharge. This label is applied to a variety of visual appearances ranging from filamentary shapes to diffuse glows, and the transient behaviour of discharges may largely depend on the external configuration. It follows that a careful insight on the physical properties of the different sequences within the discharge is needed.

The following points may however be stressed. On one side, in spite of this impressive amount of different aspects, the model offered by the low pressure glow discharge offers a satisfying model to elucidate the concept of corona discharge and its transition to sparks. On the other side, differences between low pressure and high pressure discharges gives the specificity of high pressure discharges, namely:

- Space charge may develop much more than in the low pressure case since the cathode source of electron may be far away in terms of electron mean free path.
- Thermal effects are more accentuated, because the thermal conductivity does not follow a pressure scaling law similar to discharges. Hydrodynamic expansion may thus be triggered in localized discharge regions leading to significant changes in the neutral density N, and consequently in the E/N ratio.

Within this frame, we want to focus on three different specific aspects of DC corona triggered phenomena present in corona controlled plasma generation.

Concerning the Ion Drift Region

1. Corona discharge always contains a unipolar region of ion drift. This region may greatly contribute to particle and dust charging effect and may stabilize the discharge by retarding the spark formation. However, it may also be considered as an energy sink as far as the objective is to trigger some chemical reactions aimed towards pollutant transformations.

2. On the other hand, the ions trigger overall neutral movement, the "electrical wind", due

to momentum transfer collisions. This phenomenon may sustain an efficient mixing and a low cost transport of the various species created by the ionizing discharge region, such as dissociated compounds, radicals and excited species.

Concerning the Active Transient Ionization Region

The glow to arc transition, which generally leads to a strong energy dissipation through the spark phase, may be controlled and damped in such a way that an "averted spark" non-thermal plasma is built. Within such plasmas, the ratio E/N may be changed, if not controlled, so that the degree of gas dissociation, excitation and chemical reactivity may be changed within large proportions.

This glow-to-plasma formation is reached differently, according to the polarity of the stressed electrode.

In the case of a positively stressed point electrode the controlled plasma formation in air is triggered via a conducting air filament built up by the propagation of a streamer ionizing wave. This holds for pressures ranging from some 100 Torr up to several atmospheres. Within this filament, three main processes may be identified. Electron attachment tends to stop the discharge. Meanwhile, the filamentary channel is heated, leading to a hydrodynamic channel expansion with an associated decrease in N, until ionization overpasses attachment. This arises when E/N is above a threshold value, allowing the discharge to restart. A plasma is then formed whose features are controlled by the external circuit. Spectroscopic evidence will be given to demonstrate this property.

In the case of negatively stressed electrodes, streamer formation appears only at the ultimate spark phases. The first step is the development of a continuous glow. This regime appears within the range going from the Trichel pulse regime to the spark formation. A progressively heated channel between the electrodes is formed, within which spark formation may take place. One striking feature is that less current and energy is involved in this spark phase formation compared to the positive case.

Each of these phases may have their specificities regarding their efficiency for pollution control applications.

MILITARY APPLICATIONS

APPLICATION OF PLASMA TECHNOLOGY FOR MILITARY AIR PURIFICATION APPLICATIONS

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The US Army Chemical Research, Development and Engineering Center (CRDEC) has recently conducted an evaluation of plasma technology for military air purification applications. Plasmas offer several advantages over the standard filtration approach, activated impregnated carbon, in that all known military chemical and biological warfare agent can be decontaminated by passing through a plasma reactor. Initial plasma chemistry studies have shown, however, that in certain cases toxic products can result even when the plasma reactor is challenged by non-toxic vapors. The CRDEC-sponsored technical evaluation of plasma air purification technology identified the reaction product and several other areas for futher work required to mature plasma reactors for potential military application. These areas will be reviewed along with background for evaluation of candidate air purification technologies.

APPLICATION TO MOBILE SOURCES

SIMULTANEOUS REMOVAL OF NO_X, CO_X, SO_X AND SOOT IN DIESEL ENGINE EXHAUST

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The authors have been investigating the elimination of pollutants from the exhaust of diesel engine vehicles by employing plasma reactors since 1979. As well known, exhaust gas recirculation (EGR) techniques have been examined as a means of eliminating the NO_X component because of the difficulty in utilizing a catalyst due to the large quantity of soot included in the exhaust gas from diesel engines which damages the catalyst's function.

The major reason for the reduction of the NO_X component by the EGR system is considered to be due to the lowering of the combustion temperature in the engine cylinder. Consequently, the combustion efficiency is decreased, thereby increasing the formation of soot. The engine output decreases and fuel consumption increases; even the EGR rate is adjusted in accordance with the cruising speed or load conditions. Thus, ordinary NO_X reduction techniques sacrifice the engine performance as well as increasing other pollutants; in particular, the soot. Also, the soot in the EGR branch damages the performance of engine oil.

To eliminate the soot in the EGR branch, the authors employed a system which consisted of a mechanical filter and a cyclone collector combined with an electrical collector which we named a "cyclone-cottrell collector". The idea was based on the elimination of large size soot by the cyclone collector mechanically, and smaller size particulate by the cottrell collector electrically. In practice, however, not only the soot was successfully collected in the bottom of cyclone collector, but also the NO_X component was reduced, although there were several points to be improved under practical driving conditions; for instance, the re-exhaust of the soot and the break of the wire electrode in the cottrell collector.

In order to overcome these shortcomings of the cyclone-cottrell collector, the authors began to mount a plasma reactor in various configurations downstream of the engine exhaust by focusing our attention to the fact of the reduction of the NO_X component by a plasma. In this case, the elimination of the soot was out of the consideration as no EGR system was employed. The NO_X reduction was the most severe and urgent subject to be solved. Fortunately, by this turn, not only the NO_X reduction but also CO_X and SO_X reduction became available without EGR.

New Approach to Soot Elimination :

After successfully eliminating the NO_X, CO_X, and SO_X components by using not the EGR but a plasma reactor, the authors again turned their attention to the elimination of soot in the diesel exhaust gas from the point of view of suppressing the unpleasant black smoke and thereby decreasing one of the sources of air pollution.

The authors have now successfully developed a novel and extremely effective method of eliminating soot and reducing NO_X, CO_X and SO_X simultaneously by combining discharge plasma techniques and oil dynamics.

A discharge plasma is essential in order to give the oil a dynamic structure by which the oil is efficiently used in the sprayed form for soot trapping. On the other hand, the oil dynamics is also effective for generating a uniform discharge plasma along the plasma reactor axis; i.e., the discharge plasma and oil dynamics are strongly interdependent. The construction of a plasma reactor employed in this experiment is as follows: The inner electrode was fabricated from stainless-steel rod of 6 mm diameter and 300 mm long. A screw of 1 mm pitch was cut on its surface. The outer electrode was aluminum foil wrapped around on its surface. The inner diameter of the glass tube was 16.5 mm, and outer diameter, 20 mm. Thus the gap length in the radial direction was 5.4 mm.

The discharge current flows in the radial direction in this gap and terminates to the outer electrode through a glass-tube wall that is 1.6 mm thick. In this experiment, 120 plasma reactors were used in parallel. Only an AC power supply can be used with such a discharge reactor, which has a dielectric barrier between metallic electrodes. A leakage transformer for operating a neon sign tube, 50 Hz, 100 V-15 kV, 20 mA of maximum current was used. Twenty-four leakage transformers were employed in parallel for driving 120 plasma reactors. If the elimination degree of NO_x, CO_x, SO_x will be settled lower than the maximum ability of the reactor, the number of reactors and transformers can be reduced.

The soot was eliminated almost 100% on the measuring base with a Bosh smoke tester, while 70% of the NO_x and SO_x components and 20% of the CO_x component were removed at a rotational speed of 1200 rpm (about 30 km/h) and a load of 7 kg-m (the maximum torque at 1200 rpm is about 11.4 kg-m), corresponding to about 60% of full load of a 2-L diesel engine car.

In this paper, we describe (1) the principle of the new idea for pollutant reduction by means of a combination of discharge plasma and oil dynamics, (2) the structure of our new plasma reactor, (3) experimental results on soot elimination and NO_x, SO_x and CO_x reduction.

Typical numerical summary is as follows: (1) The input power to 120 reactors at 12 kV was 1530 W; (2) The energy given to the exhausted gas was 76.5 kJ/m^3; (3) NO_x reduction efficiency is 0.75 kJ/m^3 ppm; and (4) The energy consumption for soot collection is 1.5 kJ/mg.

As a further investigation, the authors are trying a treatment of the exhaust gas from a gasoline engine in order to check the ability of our plasma reactor whether any-kind, every density, and every temperature of inlet gas can be treated into non-pollutant one or not. The up to date result concerning this will also be introduced.

INDUSTRIAL SCALE TESTS OF FLUE GAS TREATMENT

APPLICATION OF E-BEAM TREATMENT TO FLUE GAS CLEANUP IN JAPAN

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At the present time, there are three (3) projects utilizing electron beam processing of gases in Japan. One is at the Ebara Corporation research facility in Fujisawa, another is at Chubu Electric Power Co., Inc. in Nagoya, and the third is at a Tokyo Metropolitan tunnel.

The Fujisawa test facility is a 1,500 Nm^3/h simulated flue gas and incinerator gas process plant for the purpose of testing various methods to fine tune the electron beam process for commercial use. Various tests have been performed, and will be performed through 1992 to prevent or remove duct clogging by the byproduct. Additional testing was performed on diesel truck exhaust gases and incinerator gases.

The Chubu Electric facility is a 12,000 Nm^3/h test plant designed to treat various SO_x and NO_x concentration gases. This installation has its own boiler and can adjust the pollutant concentration of the flow gas. Investigation to be performed are process optimization, confirmation of system and each equipment reliability, and byproduct handling and utilization studies.

The Tokyo tunnel project is a 50,000 Nm^3/h test facility to test the process on low NO_x exhaust gases from a vehicle tunnel under Tokyo Bay. Studies will be made to optimize a high flow and low pollution concentration gas treatment system. In addition, the gases will be analyzed for other hydrocarbons to determine the effects of the electron beam process on unburned hydrocarbons.

All three projects utilize electron beam accelerators and various collector systems appropriate for their own process. They also incorporate state of the art process vessel configurations to achieve maximum removal efficiencies with minimum input energy.

This paper will discuss the plant details, the test programs and the results to date from the three projects.

INDUSTRIAL APPLICATION OF PULSED CORONA PROCESSING TO FLUE GAS

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Among the advancing new technologies for the removal of nitric and sulfuric oxides from flue gases, a very interesting process is based on the energization of the gas with electrons having energies in the range from 5 to 20 eV. The free electrons are generated in the gas by the high electric field produced by the space-charge fields on the heads of plasma filaments that start from a wire and reach a plate in a wire-plate electrode geometry. The plasma filaments are induced by applying a pulsed voltage between the wire and the plate,

The electrons induce in the gas ionization, dissociation and excitation processes, resulting in the production of active radicals (O, OH HO_2). The radicals react with NO and SO_2, and convert these partially into nitric and sulfuric acids and into NO_2. The injection of a basic compound (like ammonia) neutralized the acids to form salt particulates that can be removed by a conventional electrostatic precipitator.

The main features which make this process attractive are the following:

- combined removal of SO_2 and NO_x with a single dry process;
- a lower cost than traditional $DeNO_x$-$DeSO_x$ systems;
- its integration in existing electrostatic precipitators;
- the potential use of the by-products as fertilizers.

In this paper an experimental plant and its results are reported.

The complete process has been investigated with a test rig installed in slipstream of the flue gas duct f a coal power plant. The test rig has a wire-cylinder electrode structure, and is able to treat 100 Nm^3/h nominal gas flow rate.

For industrial applications it is preferable not to use bag filters. However, the results obtained show that the removal efficiency for NO_x is very low in the absence of excess of ammonia and heterogeneous phase reactions. In order to overcome this inconvenience the process is split into two steps. The first step is used principally for NO_x removal using a very high ammonia concentration. The second step is used to remove SO_2 and ammonia.

In order to verify the efficiency of the process, the energy consumption, the ammonia slip, and to optimize the operating conditions, experiments were carried out by energizing the flue gas with different SO_2 and NO_2 concentration at different temperatures.

Also important is the voltage pulse length and the distance between the wire and the plate. The geometry of the emitting electrode does not influence the removal efficiency.

The results of the experiments showed that it is possible to achieve a removal efficiency of about 99% for sulfur oxides and about 60% for nitrogen oxides. The ammonia slip is less than 1 ppmV. The integration of this $DeNO_x$-$DeSO_x$ process in an electrostatic precipitator also enables the increase of the efficiency of fly ash collection.

The chemical composition of the by-products show that it is possible to put them on the ammonium sulfate market without any chemical processing.

When an industrial size power plant is fitted with this $DeNO_x$-$DeSO_x$ process, an economic analysis shows that the process application overall cost is about 7.5×10^{-3} U.S. dollars for each kWh of electric energy produced by the power plant.

ELECTRON BEAM PROCESSING

CHEMICAL KINETICS MODEL OF SO_2/NO_x REMOVAL BY ELECTRON BEAM

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The electron beam treatment of polluted off-gases involves very different physico-chemical mechanisms like energy absorption, gas phase reactions, particle formation, and heterogeneous gas-solid interactions under non-equilibrium conditions. In order to understand the kinetics of the process, to interpret the experimental results, and to predict economic alternatives or novel applications, the AGATE code has been developed at KfK. The code uses literature data for the formation of primary reactive species due to electron irradiation and for the chemical reactions initiated by the primary species. Different dose rate vs. time profiles can be preset (constant dose rate, Gaussian profile, experimental profile, pulsed irradiation) to calculate the temporal behaviour of input species, reactive intermediates, and reaction products. The dependence of the final calculated gas composition on the dose or other selected input parameters is directly comparable with experimental results. The sensitivity analysis of the reaction scheme provides information about the general mechanism, about important intermediates, about the importance of reaction conditions (e.g. dose rate effects, relative humidity effects) and also about the kinetics of certain reactions. Some of these results are directly related to practical applications, while others are interesting from the point of view of basic research.

This paper describes the structure of the AGATE code and discusses the importance of the various physico-chemical steps involved in the electron beam treatment of flue gases.

$$^{15}NO + ^{14}N \rightarrow ^{15}N^{14}N + O$$

$$^{15}NO + ^{14}NH_2 \rightarrow ^{15}N^{14}N + H_2O$$

The experiments using ^{15}NO and $^{15}NH_3$ are now continued to reveal the mechanisms of the reactions of NO_x removal in the process.

Characteristics of Reaction of NH_3 with SO_2 Without Electron-Beam Irradiation

In the process of electron-beam treatment of flue gas, gaseous ammonia is added into the flue gas just before electron-beam irradiation, and a part of SO_2 in the flue gas is removed through the reaction with ammonia without electron beam irradiation. Experiments were done to clarify the characteristics of the reaction. In the experiments, gaseous mixture of 300-1800 ppm SO_2, 225 ppm NO_x, 10% O_2, 10% CO_2, 80% N_2 (dry base) and 0-20% H_2O was charged into a glass-made reaction vessel of 1.7 litter volume set in a temperature-controlled oven and gaseous ammonia was introduced into the vessel independently through another pipe. As the results, SO_2 of the gaseous mixture reacted with ammonia in the vessel, leading to the decrease of the concentrations of SO_2 and ammonia, and deposition of white powdery material on the inner surface of the vessel. From the observations in the experiments, it was found that the reaction proceeds on the surface of the reaction vessel at the temperature below 70 ^{0}C in the presence of water vapor. The fact that the mol ratio of NH_4^+/SO_4^{2+} was determined to be as small as about 1.6 in the water solution dissolved the products deposited on the inner surface of the vessel indicates that the products of the reaction consist of not only $(NH_4)_2SO_4$, but also other materials such as NH_4HSO_4. Further experiments should be done to make the mechanisms of the reaction clearer.

Enhancement of NO_x/SO_2 Removal Efficiencies

Enhancement of removal efficiencies for NO_x and SO_2 is an important subject to reduce the cost of the flue gas treatment process. Multi-stage irradiation was tested by using gaseous mixture, simulated flue gas from a coal-burning boiler, to get higher removal efficiency. In the triple-stage irradiation test, flowing gas (500 ppm SO_2, 150 ppm NO_x, 6% O_2, 14% CO_2, 80% N_2 (dry base), 12% H_2O) with 1100-1150 ppm ammonia was irradiated three times in the 1st, 2nd and 3rd irradiation chamber with twice interruption of the duration of 0.1 sec. It was found that higher NO_x removal efficiency could be achieved by double- and triple-stage irradiation. The observed effect of the multi-stage irradiation may occur through the conversion of some intermediate products, which would reproduce NO_x in the single-stage irradiation, to stable forms in the interruption between irradiations in the multi-stage irradiation. Irradiation test was performed at lower temperature of gas to get higher removal of SO_2 with lower dose. The obtained results showed high SO_2 removal of over 90% was achieved by the irradiation of the dose less than 10 kGy at the gas temperature of 65^{0}C.

The triple-stage irradiation at lower temperature will be tested in the pilot-plant, which is now under construction in Nagoya, Japan, for treatment of flue gas from coal-burning boiler to make the process more economical.

EXPERIMENTS ON CHEMICAL REACTIONS IN ELECTRON-BEAM-INDUCED NO_x/SO_2 REMOVAL

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Irradiation with electron beams was proposed as an effective method for removing nitrogen oxides (NO_x) and sulfur dioxide (SO_2) in flue gases from industrial plants such as power stations and steel plants. In this process, electron-beam irradiation causes conversions of NO_x and SO_2 to aerosols which can be collected by electrostatic precipitators or by bag filters. From the results obtained by basic studies and pilot-plant tests which have been done in Japan, Germany, the USA, etc., the process is considered to have a potential to be a simultaneous NO_x/SO_2 removal method without production of waste water to be treated. Three pilot plant tests are now being conducted for electron-beam treatment of flue gas in Japan: (1) for removal of NO_x and SO_2 from flue gas from a coal-burning power plant, (2) for removal of NO_x, SO_2 and HCl from flue gas from a municipal waste incinerator, and (3) for removal of NO_x from exhaust gas from a car-tunnel. A pilot plant is now under operation in Poland for removal of NO_x and SO_2 from flue gas from coal-burning boiler.

In parallel with the above-mentioned pilot scale tests, the reaction mechanisms of NO_x/SO_2 removal in the process have been studied by electron-beam irradiation experiments and computer simulation methods. To make the reaction mechanisms clearer and to make the removal efficiency higher, basic studies are being continued.

Experiments using gaseous mixture done in JAERI showed the experimental evidence of the conversion of NO_x to nitrogen molecules and characteristics of the reaction of SO_2 with NH_3 without electron-beam irradiation, and that enhancement of NO_x/SO_2 removal was achieved by multi-stage irradiation at lower temperature.

Formation of Nitrogen Molecule

Sufficient material balance for NO_x was not obtained with the detected amounts of ammonium nitrate and dinitrogen monoxide as nitrogen-containing products in the electron-beam irradiation of gaseous mixture of which components were close to that of real flue gas. From the results and basic data on related reactions of NO_x with N atoms and NH_2 radicals, it was assumed that a part of NO_x might be converted to nitrogen molecules in the process. Irradiation experiments using gaseous mixture containing ^{15}NO were done to detect the formation of nitrogen molecules in electron-beam irradiation of the gas. When the gaseous mixture of 400 ppm ^{15}NO, 1720 ppm SO_2, 6.9% O_2, 92.5% N_2 (dry base), 13% H_2O with 3840 ppm ammonia was irradiated with electron-beam with the dose of 14 kGy at 80 °C, 90 ppm increase of the concentration of $^{15}N^{14}N$ was observed in the irradiated gas. The fact indicates that 23% of 400 ppm ^{15}N was decomposed to form nitrogen molecules by electron-beam irradiation. That is, NO_x is converted not only to NH_4NO_3 and N_2O, but also to nitrogen molecule by electron beam irradiation in the process. From the results obtained by the experiments of electron-beam irradiation of gaseous mixture containing ^{15}NO and/or $^{15}NH_3$, the formation of nitrogen molecules was found to proceed through the reactions of NO with N atom and NH_2 radicals produced by electron-beam irradiation of the mixture as follows:

SO_2 AND NO_x REMOVAL FROM FLUE GAS BY MEANS OF LIME SPRAY DRYER FOLLOWED BY ELECTRON BEAM IRRADIATION*

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When a high energy beam of electrons is directed into flue gas, abundant quantities of radicals and free atoms are generated. The radicals and atoms containing oxygen react with SO_2 and NO_x to form acids. These acids can be removed by reaction with an alkali to form solid salts. These reactions are enhanced by high humidity, low temperature flue gas. A lime slurry spray dryer can be used in order to achieve these gas conditions and to supply the required alkali. In this method the flue gas first passes through a spray dryer, where the gas is cooled and humidified by means of slurry evaporation, and hydrated lime in the form of fine particulate is entrained by the gas. Approximately one-half of the SO_2 reacts with the calcium hydroxide in the spray dryer to form calcium sulfite. The gas is subsequently irradiated by an electron beam which results in the conversion of SO_2 and NO_x to sulfuric and nitric acid. The gas finally passes through a fabric filter in which the acids react with calcium hydroxide to produce calcium sulfate and nitrate. These products, as well as entrained fly ash are removed by the fabric filter.

In order to evaluate this concept and to provide design guidelines for commercial scale applications, a pilot scale spray dryer, electron beam, fabric filter system was operated at the TVA Shawnee Steam Plant in Paducah, KY. The pilot scale system processed a 4000 acfm slipstream from a 150 MW coal-fired boiler. A 100 mA continuous beam of 750 kV electrons was used, yielding absorbed dosages of up to 2 Mrad.

The objectives of the test program were to determine the relationships between SO_2/NO_x removal and electron beam radiation dose, gas temperature, gas humidity, SO_2 concentration and lime usage, and to evaluate the economic viability of a commercial scale electron beam system. This paper describes the experimental results. A phenomenological model is proposed which accurately predicts experimental results, and an economic analysis is made, which compares this system with more conventional flue gas cleanup systems.

*This work was performed at the TVA Shawnee Steam Plant under the auspices of the U.S. Department of Energy under Contract No. DEFC22-81PC15079.

RESEARCH ON ELECTRON BEAM FLUE GAS TREATMENT IN POLAND

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Two research installations, one laboratory and second industrial pilot plant, have been constructed in Poland.

The laboratory unit for electron beam flue gas treatment has been built at INCT. Two gas-fired boilers generate flue gases of volume flow up to 400 Nm^3/h. The composition of the gas can be adjusted by additional injection of the impurities whose reduction is investigated. Ammonia and water can be added to the gas stream before the reaction vessel. The ILU-6 accelerator is used (electron energy of 600-1000 keV) as an irradiator. The post-radiation aerosol is removed from the gas by a fabric filter. The installation is employed to perform experiments concerning electron beam/microwave combined field applications. It is also applied to analytical methods calibration and tests on different filtration fabric. It is also applied to the degradation of volatile organic compounds in flue gas.

The Polish pilot plant for electron beam SO_2 and NO_x removal from flue gas has been constructed at the Electropower Station in Kaweczyn. The gas flow capacity is 20,000 Nm^3/h, and it is the biggest operated industrial plant using this technology. The installation was built on the bypass of the main gas stream (25,000 Nm^3/h) of the boiler WP-120. As a fossil fuel coal of sulfur content equal to 0.8 - 1% is used. In the spray cooler flue gas is cooled to 70 - 90 ^0C and then ammonia, in substoichiometric quantities, is added. The mixture is treated by electron beam and solid product, being a mixture of ammonia sulfate and nitrate, is removed in a bag filter.

For the first time in an industrial installation, step-by-step irradiation was applied. This arrangement decreases the energy consumption in comparison to a one-step irradiation unit.

Two point continuous monitoring system was used for SO_2, NO_x, NO_2, O_2 and fly ash concentration measurements. The PC data acquisition system collects and records data from all measurement points.

The results of the industrial tests have proven that application of two-stage irradiation causes remarkable power reduction for NO_x removal at high process efficiency.

The model of the process based on chemical reaction theory has been elaborated. This model was applied for data correlation, obtained on the Polish pilot plant and laboratory installations in KfK and JAERI.

INVESTIGATION OF SO_2 OXIDATION IN HUMID AIR STREAM BY HIGH CURRENT DENSITY PULSE ELECTRON BEAM

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The electron beam and impulse corona discharge technology of air flow purification from SO_2 and NO_x are investigated now in many countries. One of the main problems facing the practical use of these methods is the reduction of the oxidation energy cost. So in case of purification of flue gases with SO_2 concentration 0.1% and conventional oxidation energy cost 10 eV per one molecule, it is necessary to have more than one hundred 100 kW accelerators to clean exhaust gas from a 300 MW electric power plant. In the work of Potapkin *et al.*, it was proposed that the oxidation energy cost can be significantly reduced in humid air at a definite range of EB current density because of the realization of chain, ion-molecular SO_2 oxidation mechanism. This work is concerned with the experimental and theoreti.oal investidation of energy cost dependence of SO_2 oxidation versus electron beam current density and air humidity. The main objective of this work is to find the low energy cost SO_2 oxidation regime.

Experiments were carried out on two experimental setups with different regime of EB generation: pulse system with closed reaction volume and pulse-periodic flow EB system. Pulse EB experiments were made in air mixture containing 1% SO_2, 3.4% H_2O at room temperature and the concentration of water steam remained constant during the experiment. EB current density (pulse duration 10 s) was changed from $1.5 \pm 0.5 \times 10^{-2}$ A/cm^2 to 10^{-2} A/cm^2. Within experimental errors the oxidation energy cost was proportional to the root of the current density. The minimum value of energy cost of SO_2 oxidation was 3.2 ± 0.8 eV at current density of 1.5×10^{-2} A/cm^2. This indicates the realization of chain oxidation mechanism. Moreover theoretical analysis show that the root dependence of the energy cost can be explained only if ion-molecular chain processes are assumed. The possibility of chain oxidation processes was confirmed by the experiments with pulse-periodic EB flow system. The current density of the electron beam was 10^{-2} A/cm^2, the flow rate was changed from 3 cm^3/s to 10 cm^3/s. The temperature of the air mixture of the same composition was up to 40 ^{0}C. In accordance with the results of the pulse experiments, the oxidation energy cost was 2 eV per molecule. It was shown also that chain effect can occur only if air humidity is close to 100%.

Thus the results of this investigation confirm the possibility of ion-molecule chain mechanism of SO_2 oxidation in gas phase and reduction of purification energy cost of air streams.

REMOVAL OF VOLATILE HYDROCARBONS FROM INDUSTRIAL OFF-GAS

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During recent years emissions from fossile fuelled power plants have been significantly reduced in industrialized countries. However only little progress has been made for emissions which are low in concentration and contain several components (organic, inorganic and aerosols). Quite often these emission are characterized by large volumes, which is due to specific process requirements. Typical off-gases of this kind are emitted from industrial processes (e.g. coating of metal parts with solvent containing paints) and from automobile tunnels. The cleaning of these cold off-gases by conventional methods requires high investment and operating costs due to their energy consumption. Therefore major process modifications (primary measures) and novel off-gas cleaning methods are necessary to reduce these pollutants.

Electron beam irradiation provides a simple and safe method for the simultaneous removal of organic traces from off-gas. By electron beam irradiation OH-radicals are produced in the off gas, which subsequently oxidize the pollutants.

This paper describes experimental and theoretical results, suitable to determine the removal efficiencies and energy consumption of electron beam induced cleaning of dilute emissions of Volatile Organic Compounds (VOC). The range of application of the process will be discussed and compared to other conventional clean-up methods.

UV AND EB DEGRADATION OF CHLORINATED HYDROCARBONS AND AROMATICS

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Various volatile pollutants can be degraded by electron-beam (EB) irradiation or UV-photolysis in the gas phase. A gas flow system handling such vapours is installed at an irradiation unit consisting of an excimer UV lamp and a low-energy electron accelerator. The main characteristics of the irradiation sources used are as follows:

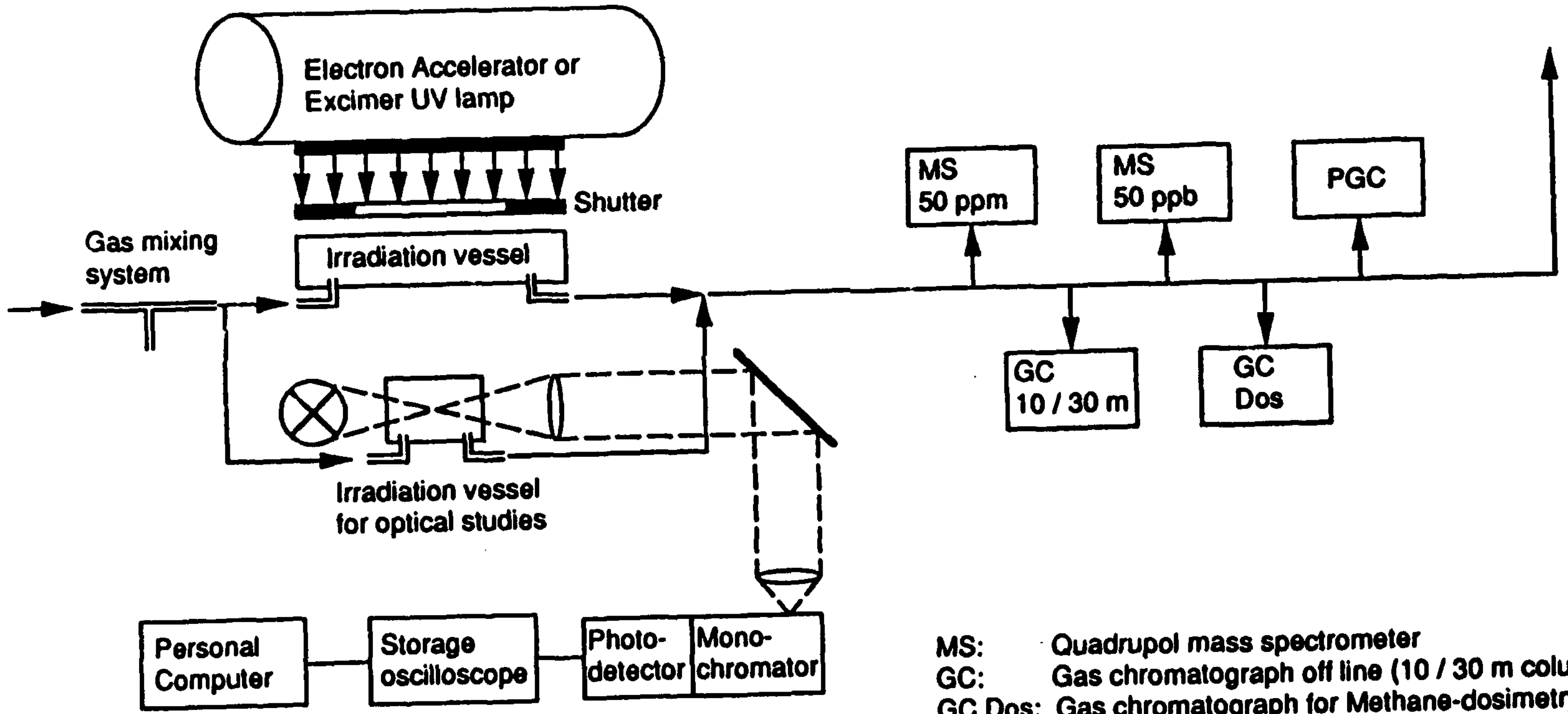
- low energy electron accelerator
  energy: 150 - 200 keV, beam power: 0.5 - 20 W/cm^2

- incoherent excimer UV-lamp
  KrCl (222 nm), UV intensity: up to 0.3 W/cm^2

Gas phase photolysis or radiolysis can be monitored under continuous flow conditions, using quadrupole mass spectroscopy, gas chromatography and optical spectroscopy as detection methods (Figure 1).

The decomposition of chlorinated hydrocarbons and aromatics, e.g. trichloroethylene, vinyl chloride, benzene and toluene, was studied, varying the irradiation and gas flow conditions. First results concerning rates and degree of decomposition under the action of UV and EB exposure are presented. Technological aspects of both alternative decomposition procedures are discussed.

Degradation of Chlorinated Hydrocarbons Gas Phase Radiolysis and Photolysis Set-up



MS: Quadrupol mass spectrometer
GC: Gas chromatograph off line (10 / 30 m column)
GC Dos: Gas chromatograph for Methane-dosimetry
PGC: Process chromatograph on line

Figure 1

DC DISCHARGE PROCESSING

GLIDING DISCHARGE REACTOR FOR H_2S VALORIZATION OR DESTRUCTION

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Hydrogen sulfide is present in the fluids issuing from the ground and in industrial gases. It has always been sought to destroy this pollutant and possibly to valorize it. Various processes have been used for treating H_2S. The hydrogen is weakly bound to the molecule and this fact is the main downfall in the classical Claus process in which the hydrogen becomes transformed into water and lost for all desulfurization or hydrogen energetics. Moreover the process cannot be sustained if the CO_2 concentration in the gas exceeds 60%. Other processes lead to the diluted H_2S destruction but they require considerable volumes of apparatus subjected to corrosion. They present the further drawback of consuming a considerable amount of chemical reagents and raising environmental problems created by the final products.

The only way for H_2S total valorization and/or destruction goes through a direct use of electrical processes at atmospheric pressures. Radio-frequency, microwave and capacity-type discharges through H_2S were already described but none of them could have an industrial application because of costs, product separation, low pressure use, and limitations in industrial size power supplies.

We are developing new energy efficient and industrial size plasma reactors based on relatively high current gliding discharges at atmospheric pressure. At least two diverging electrodes are placed in a fast gas flow and in the flow direction. Gliding discharges are produced between the electrodes and across the flow. A fast displacement of the discharge on electrodes prevents their corrosion by usually high current arc establishment so we can easily process or overheat every kind of gas or vapor, cold or hot, at a flow-rate up to 4,000 m^3/h and at a power up to 250 kW. The electrical energy is directly and totally transferred to the processed gas. The average voltage may range up to 10 kV for currents from 0.1 to 50 A (per couple of electrodes). The instantaneous voltage, current end dissipated electric power observed via digital oscilloscope show almost random features of the history of each gilding breakdown. This transient characteristic under atmospheric pressure is similar to glow discharge characteristics. A large ionized gas volume, obtained at low energy density, gives an out of thermal equilibrium and extremely reactive medium due to the presence of very active atomic and molecular species. This reactor (GlidArc) enables us to propose a new electrochemical gas technology in which H_2S can be processed (SulfArc) by acting at three H_2S concentration levels:

A - total abatement and complete valorization of concentrated H_2S/CO_2 mixtures,

B - total abatement and partial valorization of concentrated or diluted H_2S,

C - total abatement of very diluted H_2S.

Several tests have been performed in a laboratory scale 3- or 6electrode reactor at up to 7

m^3/h gas flow and 3 kW power.

A. In primary experiments on H_2S dissociation (pure or mixed with H_2 or Ar) to hydrogen and sulfur we have found that such a simple process cannot be efficiently performed probably due to very fast recombination of hydrogen with sulfur vapour. We propose therefore n two-step SulfArc process of total abatement and complete H_2S valorization described by two successive reactions:

$$H_2S + CO_2 \rightarrow H_2O(v) + S + CO \quad (\text{endothermic}, 0.76\ \text{kWh/Nm}^3\ H_2S)$$

$$CO + H_2O(v) \rightarrow CO_2 + H_2 \quad (\text{exothermic}, 0.51\ \text{kWh/Nm}^3\ CO)$$

The first one can be performed in our reactor. The shift reaction can then easily transform CO to H_2, the products can be separated and the CO_2 can be recycled. Anyhow the Claus process cannot be sustained if the CO_2 concentration in the gas exceeds 60% or if the H_2S concentration is less than 7%; in most cases CO_2 is accompanying H_2S in natural fluids and the two acid gases are hard to separate. In the first experiment with H_2S/CO_2 = 0.69 molar ratio at only 0.36 kWh energy input per 1 Nm^3 of gas mixture we obtained 39% H_2S transformation. It means that as much as 32% of input energy was used to drive the endothermic reaction (a possible heat recovery is not taken into account) giving a specific energy expense as low as 2.2 kWh/Nm^3 CO.

B. Our experiments show that it is very easy to completely "burn" the diluted H_2S contained in air, CO_2 or steam to SO_2, with the H_2S concentrations even much lower than the limit of flammability. The SO_2 can then be valorized to sulfur via a catalytic reaction with H_2S. Such an electrically assisted low-temperature H_2S incineration avoids any fuel (and extra air with N_2 ballast) addition, and a higher stem concentration in combustion products. In a series of experiments the electrical energy expense was 0.14 kWh for complete incineration of 1 Nm of air containing 0.7% H_2S, or 0.17 kWh when a mixture of 1.2% H_2S + 65.4% CO_2 + 33.4% air was treated (without any preheating). Sulfur was precipitated from polluted geothermal steam contained 3.6 g H_2S and 236 g CO_2 in 1 kg of fluid without air addition when 0.23 kWh of electrical energy was injected to the GlidArc reactor.

C. The stink of H_2S can be detected at less than 0.2 ppm while the threshold limit without adverse effects is 10 ppm. The product of H_2S incineration is SO_2, but the smell can only be detected at 3 ppm (toxic threshold limit 5 ppm). It is therefore suitable to transform very diluted H_2S to SO_2 in order to avoid at least an olfactory fatigue. The third version of the SulfArc can provide total incineration of the diluted H_2S (or other organic sulfur) and solve the odor nuisance via plasma assisted oxidation of such compounds to SO_2 which may be then destroyed by absorption or, if very diluted, released to the atmosphere.

The gliding electric discharges are found to reduce considerably the nuisance of existing processes of industrial depollution from H_2S. The use of such discharges brings to these processes an easily controllable energy and a flow of catalytic species (ions, atoms and radicals). High energy consuming and troublesome thermal incineration or dissociation at high temperatures can be replaced by this particularly cold and catalytic plasma assisted process at lower specific energy expense.

DECOMPOSITION OF NO_2 BY GLOW DISCHARGE PLASMA*

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Nitrogen dioxide (NO_2) is one of the most difficult air pollutants for us to get rid of chemically. Therefore, a lot of trials have recently been done to decompose it by corona discharge after exhaust in the air. As well as these trials, it is necessary to give quantitative information about the coefficients representing the fundamental collision processes of an electron, an ion and a photon with an NO_2 molecule in a uniform electric field, which is essential for designing corona discharge devices. In the present study, we measured the decomposition rate of NO_2 molecules in a uniform glow discharge and the electron impact ionization coefficient and attachment coefficient in NO_2 gas of pressures between 1 and 7 Torr. In this experiment Harrison type parallel plate electrodes were used. The decomposition process of NO_2 is discussed.

In NO_2 glow discharges with current densities between 0.15 and 0.5 mA/cm^2, with increasing discharge duration the gas pressure increased up to around 1.5 times of the initial pressure due to decomposition of NO_2. The ratio of the final pressure to the initial pressure increased slightly with increasing the initial pressure. At the same time the intensity of absorbance of NO_2 was reduced significantly compared with the intensity before the discharge. It was estimated from these results that around 85% of NO_2 molecules was decomposed. The decomposed species were revealed by a gas chromatography method as NO, N_2O. N_2 and O_2 molecules. The NO concentration increased in the initial stage of the glow discharge, and after that decreased promptly, since NO is not stable species. The concentration of N_2O was about ten times smaller than that of NO, but it did not decrease so fast as that of NO. The N_2 and O_2 concentration naturally increased with increasing the discharge duration and the current density.

In order to check the propriety of the observation made by the above methods, the concentration of NO_2 and NO was measured using a NO_2+NO detector, and the emission spectra from the glow discharge were observed as well. The obtained results were consistent to those obtained using the absorbance and the gas chromatography techniques. It was suggested that in the initial stage of the discharge NO_2 was mainly decomposed into NO and O by relatively low energy electrons, since the E/p_0 value in the glow discharge is generally relatively low. The discharge voltage at a gas pressure of 3 Torr was changed between 400 and 700 V depending on the current density, and decreased slightly with increasing discharge duration.

The measurement of the electron impact ionization and attachment coefficient in NO_2 gas in a E/p_0 range between 70 and 380 V/cm/Torr showed that the ionization coefficient in NO_2 gas was smaller than values in N_2 and 0_2 gases for E/p_0 below 200 V/cm/Torr and that the attachment coefficient was smaller than values of SF_6 while it was larger than values of 0_2. The limiting E/p_0 in NO_2 gas was given to be 95 V/cm/Torr.

*This work was performed at Hokkaido University under the auspices of a Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Culture.

NEGATIVE CORONA-INDUCED DECOMPOSITION OF CCl_2F_2*

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Corona discharges are known to produce the decomposition of various gases. That is why there has recently been an increasing interest in the application of corona discharges for a treatment of waste gases. The removal efficiencies of individual gas components from the gas mixture are very different. The removal efficiency of one gas component can be characterized by its decomposition rate expressed in terms of change in the quantity of decomposed gaseous substance per energy unit dissipated in the discharge or per charge unit transported in the discharge gap. For low-current discharges, such as corona, in which the dissociation is governed by electron collisions, the rate expressed per unit of the transported charge is more convenient. The experimental studies of many authors have shown that the decomposition rate is strongly affected by discharge parameters and depends on physical and chemical properties of the decomposed gas. There are gases for which extremely low decomposition rate in negative corona is typical (CH_4, SF_6). On the contrary, very large removal efficiencies were observed for CHI_3, C_6H_5I and C_2HCl_3 substances. The purpose of this work is to measure the decomposition rate of dichloro-difluorocarbon - freon 12 (CFC12) in mixtures with air induced by negative glow corona discharge. The effect of ozone presence on the decomposition rate of CFC12 was also studied.

Testing of decomposition was carried out using a cylindrical corona discharge tube of 15 mm inside diameter and 1 m long. The central electrode was a molybdenum wire of 0.1 mm diameter at constant voltage. Chemical analyses of the gas mixture were performed by gas chromatography and UV spectroscopy.

A significant removal (around 90 %) of freon molecules from the mixture of CFC12 was observed. The most striking feature was that the decomposition rate increases with increasing initial concentration of CFC12 in the mixture. The discharge current was affected by the initial concentration of CFC12 and the concentration of ozone which is generated in the discharge gap. The discharge current was decreasing accordingly with increase of ozone concentration. The saturated values of ozone concentration decreased with increase of initial concentration of CFC12 in the mixture. The observed relationship between the ozone generation and the freon dissociation implies that the reaction of ozone with the by-products of the freon dissociation have an influence on the decomposition rate of freon.

Thus from the consideration of the known attachment and bond dissociation energies of CFC12, two initial steps in the decomposition of CFC12 can be presumed:

1. dissociation attachment of electrons

$$e + CCl_2F_2 \rightarrow CClF_2^{\cdot} + Cl^-$$

which is favored for nearly thermalized electrons the drift region of the discharge gap

2. the direct dissociation of CFC12 by electron impact

$$e + CCl_2F_2 \rightarrow CClF_2^{\cdot} + Cl^{\cdot} + e$$

followed by reactions of Cl' radicals with ozone molecules

$$O_3 + Cl^{\cdot} \rightarrow ClO^{\cdot} + O_2$$

$$ClO^{\cdot} + O \rightarrow Cl^{\cdot} + O_2$$

The direct dissociation is dominant in the vicinity of the central wire electrode where the energies of electrons are above the C-Cl bond dissociation energy ≈ 4.5 eV.

Our experiments suggested some analogies between observed phenomena in corona discharge and the phenomena of ozone destruction in the stratosphere caused by emission of freon into the atmosphere. The large efficiency of negative corona discharge for removal of freon traces from air observed in experiments supported the idea of employing the corona discharge for the treatment of waste gases containing chlorinated hydrocarbons.

*This work was performed at the Department of Plasma Physics of Comenius University in Bratislava under the grand support of the Slovak Ministry of Education.

SILENT DISCHARGE PROCESSING

HYDROGENATION OF CO_2 IN A SILENT DISCHARGE

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Approximately 60% of the man-made greenhouse effect is due to emissions of carbon dioxide (CO_2). Anthropogenic emissions of CO_2 amount to 8 Gtc/year (Gigatons carbon/year). Of this total about 6 Gtc are due to combustion of fossil fuels. These emissions might lead to global warming of the surface of the earth. This, in turn, could have very serious consequences for life on earth.

One of the suggested methods for mitigating increasing greenhouse gas emissions is to remove CO_2 from the flue or fuel gases of power plants. Thereupon one could either dispose of the CO_2 in the ocean or on land in empty gas wells, coal mines or salt domes. Another possibility would be to recycle the CO_2, i.e. use it again. One possible utilization of CO_2 on a large scale is the conversion of CO_2 with the aid of hydrogen to form methane or methanol. This new fuel could be used for cars or power plants and thus reduce the need for getting additional oil or natural gas out of the ground. Eventually the CO_2 molecule would end up in the atmosphere. But due to the fact, that it has been used twice, the overall emissions of CO_2 would be reduced.

In the above case capture of CO_2 from e.g. the flue gases of power stations would be necessary. ABB has already installed a CO_2-removal unit in a power plant at Shady Point in Oklahoma. At this location 200 tons of CO_2 are separated from the flue gas stream every day. The product, which is liquid CO_2 and 99.99% pure, is used in the food industry. This installation was the first removal unit of its kind in the world to be used in a power plant running on coal.

The key to hydrogenation of CO_2 is, of course, the availability of hydrogen. This hydrogen would have to be produced in a CO_2-free way, e.g. by using solar energy, hydro energy, nuclear energy or biomass and reforestation.

Today methanol is produced from carbon monoxide (CO) and hydrogen, which are derived either from coal or natural gas and steam at high temperatures (200-270 ^{0}C) and pressures (50-150 bar) by using catalysts. The production of methanol from CO_2 and H_2 is not so well known. If this process should ever be used on a large scale in connection with CO_2 derived from flue or fuel gases then lower temperatures (100-150 ^{0}C) and lower pressures (1-30 bar) would be preferable. Substantial work is needed before the appropriate catalysts for such a process can be found. The ultimate goal of this work is to contribute to the development of a thermal catalytic reactor, which works in the above mentioned range and which uses solely CO_2 as a feed gas for C and O atoms.

In the initial stages of this work we used an experimental reactor to activate CO_2 and H_2. The reactor consists of a silent discharge tube made of quartz with a metallic inner electrode, which can be cooled. A wire mesh is wrapped around the quartz tube and used as a second electrode. The silent discharge consists of a multitude of microdischarges, which serve as a source of fast electrons [1]. These electrons, which have a lifetime of only a few nanoseconds at pressures around 1 bar, excite the CO_2 and H_2 molecules present and thus initiate the reactions which lead to generation of higher hydrocarbons.

We have both used the discharge with and without a catalyst. The catalytic material was deposited on a quartz "wool" and put into the discharge gap [2]. We applied high voltage (20 kV) of high frequency (25 kHz) to a gap of 3 mm width at a pressure of 1 bar. Neither the pressure nor the gap width were changed in these initial experiments. Only the residence time was adjusted to maximize the output of the species generated.

We furthermore established a computer model of the processes taking place in such a discharge. By simulating a number of microdischarges occurring in the discharge gap and combining these with the chemical activity taking place, we could calculate the species generated both as a function of composition and temperature for a fixed time as well as their temporal development.

The modelling of the discharge behaviour is based on our experience with modelling of microdischarges for ozone generation and production of excimers in silent discharges [1]. The chemical reactions used in our model were taken from [3]. These reactions were extended by reactions specifying the dissociative interaction of electrons and molecules of the kind

$$e + CO_2 \rightarrow CO + O + e$$

We measured the carbon monoxide, methane and methanol generated in an initial mixture of CO_2 and H_2. All the experiments were performed at pressures of 1 bar and a fixed temperature. For CO_2 a maximum conversion (i.e. moles CO_2 converted/initial moles CO_2) of 10% was obtained without a catalyst. The main products and their selectivities (i.e. moles formed/moles CO_2 converted) were CO(33%) and CH_4 (67%).

By using a catalyst small amounts of methanol were generated. The catalytic material consisted of a mixture of CuO and ZnO deposited on a quartz surface. The maximum CO_2 conversion was again 10% and the selectivities were this time 28.6% (CO), 71% (CH_4) and 0.4% (CH_3OH). The conversion yields were of the order of 1g CO_2 converted per each kWh of applied energy [4]. This, of course, is far from satisfactory for an industrial process. At this stage no attempts were made to increase the yield.

These experiments were of a very preliminary nature and serve primarily as a test of the chemistry involved. The questions of efficiency and economics were not studied or considered at this point. An efficient and economic production of hydrogenated CO_2 would presumably make use of a catalytic thermal reactor.

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UV PRODUCTION IN DIELECTRIC-BARRIER DISCHARGES FOR POLLUTION CONTROL

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Recent investigations in dielectric-barrier discharges (silent discharges) revealed that in certain gas mixtures discharge conditions can be established that favour the formation of excimer or exciplex complexes [1-3]. Fluorescence during the decay of these unstable molecular complexes can lead to narrow-band ultraviolet or vacuum ultraviolet radiation. In many cases the gas mixtures can be chosen in such a way that only a single emission band of a few nm half-width is obtained. The plasma conditions can be optimized to yield UV efficiencies of the order of 10% in these narrow emission bands. So far, about twenty different excimers radiating at wavelengths between 120 nm and 560 nm have been excited in dielectric-barrier discharges. Most of them can be run at fairly high power densities like excimer lasers. Excimer lamps can be operated with sealed quartz vessels using external electrodes unlike most commercial excimer lasers. With certain excimer gas mixtures life times of several hundred hours have been demonstrated using sealed tubes.

The availability of narrow-band high-intensity UV and VUV radiation can be utilized to initiate a number of selective photochemical reactions [4,5]. Possible applications include photochemical synthesis as well as the photocleavage of pollutants such as dioxins and chlorinated hydrocarbons. While some dioxins like for example TCDD (2,3,7,8-tetrachlorodibenzodioxin) absorb UV radiation around 300 nm and below 250 nm the most abundant pollutants like TCE (trichloroethylene) and PCE (tetrachloroethylene) have sufficiently high absorption coefficients only at wavelengths shorter than 250 nm. In the range 190 nm-230 nm their absorption cross sections are of the order 10^{-17} cm^2.

Pollution control by UV radiation becomes attractive when the dilution of the pollutant is extreme. Under such conditions heating of the whole gas volume is not economic, chemical reaction rates with added oxidants are too slow and the expenditure of physical separation processes becomes prohibitive. Using ultraviolet radiation two completely different approaches can be distinguished. In the wavelength region below about 190 nm the radiation is mainly absorbed by the carrier fluid (normally air or water) and results in the formation of reactive species ($O(^1D)$, $O(^3P)$, O_2^* O_3, OH, H_2O^*, HO_2) which readily oxidize any pollutants present. Suitable excimer UV sources would be Xe_2^* peaking at 172 nm and $ArCl^*$ peaking at 175 nm. In this wavelength region the VUV radiation is used to initiate a free radical chemistry comparable to the effect of γ-radiation, electron beams or nonequilibrium gas discharges.

In the wavelength region $\lambda > 190$ nm the absorption cross sections of the pollutants can be six to ten orders of magnitude larger than those of the practically transparent carrier fluid. Consequently selective photocleavage even of extremely diluted pollutants becomes an attractive and economic possibility. Typical excimers in this wavelength region are KrI^* at 190 nm, ArF^* at 193 nm, $KrBr^*$ at 207 nm, $KrCl^*$ at 222 nm, KrF^* at 249 nm, XeI^* at 253 nm, $XeBr^*$ at 283 nm and $XeCl^*$ at 308 nm.

Special geometrical configurations combining the UV generating dielectric-barrier discharge with the photoreactor for pollution processing will be discussed. In addition, special configurations combining UV treatment with nonequilibrium discharges in the carrier gas will be presented.

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MODELLING OF DIELECTRIC BARRIER DISCHARGES

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The investigation of dielectric barrier discharges is of interest in order to understand e.g. ozone generation and the deterioration of insulating materials by partial discharges in high voltage techniques. Recently a growing number of new applications have come into focus like the decomposition of complex molecules i.e. for example the processing of flue and the removal of waste gases or the production of UV light. In all cases it is essential to understand the fundamental processes in the discharge in detail in order to assess the possibilities of this type of discharge respectively to improve efficiencies.

In general the dielectric barrier discharge is produced between flat, extended electrodes with at least one of the electrodes covered with a dielectric. Driven by AC high voltage it consists of numerous "microdischarges" temporally and spatially distributed over the discharge area. At atmospheric pressure these microdischarges last for several ten nanoseconds regardless of the frequency of the supply voltage in a wide range. The appearance of single microdischarges depends on the local field configuration which results in a self pulsing system. Each microdischarge consists of a combination of a volume discharge in the gap and a surface discharge on the dielectric.

To model these microdischarges two methods have been chosen, a one-and-a-half dimensional and a two dimensional modelling. The modellings are based on a cylindrical symmetry of the discharge for air at atmospheric pressure. A set of continuity equations is solved in connection with the Poisson equation in order to take into account space charge induced distortions of the electric field. Unknown values of drift velocities of the charged particles and reaction coefficients have been calculated from tabulated cross sections solving the Boltzmann equation with a Monte Carlo technique. Secondary electron emission from ions as well as photoemission on the cathode is taken into account.

For the one-and-a-half dimensional modelling the particles within the discharge column have been regarded as being uniformly distributed over the cross section. Assuming the lateral extension of the discharge being determined by electron drift, the radius of the discharge can be derived from experimental values. The surface discharge in the case of a dielectric anode has been taken into account by assuming that the accumulated charges on the dielectric are spread over a disc with a constant charge density.

The self consistent two dimensional modelling has been based on the coupled solution of a set of continuity equation for each particle under consideration and the Poisson equation for the potential in axial as well as in radial direction. In order to avoid numerical diffusion a flux correction technique has been applied.

From the modelling it follows that the temporal development of the microdischarge can be divided into four phases, i.e. an initial Townsend phase, a cathode directed ionization wave or streamer phase, a cathode layer formation phase and a decay phase. The cathode layer formation as well as the phenomena at the dielectric anode are studied in detail. The diameter of the cathode layer defines practically the size of the discharge channel if the cathode is of metal. The rate of rise of the external current is connected with the velocity of the extension of the cathode layer area. After the formation of the cathode layer all distributions within the discharge column are nearly frozen. Confirmed by experimental results an "active region" is shifting along the dielectric surface which is able to dissociate, excite, and respectively ionize. For an example the importance of different phases and portions of the microdischarge is discussed. Electron, field strength and energy density distributions are presented. Quantitative results for the ozone generation process are given and compared with experimental findings.

DIELECTRIC-BARRIER DISCHARGE FOR PROCESSING OF SO_2/NO_X

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We report the results of an investigation of plasma assisted oxidation of SO_2 to SO_3. The SO_3 is a more desirable byproduct of flue gas as opposed to SO_2 because it can be dissolved in water easily and can be reacted with lime to form gypsum. A co-axial dielectric-barrier discharge is used to generate an air plasma to carry out the reaction. The dielectric-barrier discharge, which is an interrupted discharge, is very efficient in producing atomic oxygen and requires a simple form of excitation.

Since the microdischarges in the dielectric barrier discharge are best characterized as streamers, the typical electron density at atmospheric pressure is of the order of 0.5×10^{14} cm^{-3}. The typical duration these streamers last for is of the order of 2 - 10 ns for a 1 cm length gap. Using a plasma chemistry model, simulations were carried out to study the time evolution of the species and the effect of UV-irradiation on the species population. The simulations suggest that with adequate residence time (100 μs) over 96% of the SO_2 is oxidized to SO_3, and NO and N_2O are completely reduced to N_2. Furthermore, the UV-irradiation in low level is very effective in dissociating ozone, produced in the discharge, to atomic oxygen. This enhances the oxidation of the SO_2 and over 99% removal can be achieved with 10 W/cm^2 of UV-irradiation and residence time of the order of 10^{-3} s.

The experimental work was carried out in a discharge chamber which consists of a stainless-steel center electrode, a glass dielectric, and an aluminum outer electrode. From oscilloscope traces it was observed that the microdischarges appear on the rising edge of the voltage waveform and as the dielectric charges up the discharge is quenched. The negative going pulse discharges the dielectric and the cycle repeats.

The experiments were done at room temperature for a pressure range of 650 to 760 Torr, total flow rates in the range of 1550 SCCM to 3500 SCCM, and SO_2 concentration in the range of 300 ppm to 14,000 ppm. The concentration of oxygen in the reactor plays an important role in the removal of SO_2. The SO_2 is oxidized to SO_3 by a three body reaction involving oxygen atom which is produced in the discharge by electron impact dissociation. The production of ozone is a competing mechanism for loss of oxygen atoms. The addition of oxygen molecules increases the oxygen atom concentration. This initially increases the percentage of SO_2 removal. However, further increase in O_2 concentration favors ozone formation and thus depletes the atomic oxygen concentration. At high O_2 concentration, the rate of SO_3 formation becomes independent of the O_2 concentration.

We also studied the effect of SO_2 concentration on SO_2 removal. Since SO_2 is an attaching gas, at high concentrations it reduces the electron density which results in the lowering of SO_2 removal at high SO_2 concentration. At low SO_2 concentration, the percentage of SO_2 removal is high.

Emission spectra from a dielectric-barrier discharge in pure O_2, and O_2 and SO_2 mixture were obtained. The oxygen atom emission line at 7775 Å clearly shows a reduction in intensity with the addition of SO_2.

The proposed method is a novel, viable and efficient means of SO_2/NO_x removal from combustion and conversion facilities. It is applicable over a wide range of pressure and temperature, and does not require any material regeneration, which is a major advantage over solid sorbents. The plasma produced by a simple voltage transformer at 60 Hz (power supply voltage) is an effective and cheap source of plasma to carry out gas-phase reaction of SO_2 and NO. The simultaneous removal of NO_x will make this an attractive alternative to other flue gas clean-up methods.

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DECOMPOSITION OF COMPLEX MOLECULES USING SILENT DISCHARGE PROCESSING

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Investigation of the use of Silent Discharge Plasma (SDP) for removal of oxidizable pollutant compounds from air and other oxygen containing carrier gases has been conducted in these laboratories since 1984. As used here, the term SDP refers to a discharge occurring in an open space between two insulated electrodes connected to a source of high voltage alternating current. A glowing plasma appears between the insulating surfaces. It appears to emit a continuous glow but in reality arises from a very large number of microdischarges of short lifetime but high instantaneous current which are generated by discharges from small discrete regions in the insulators. The electron temperatures in the discharge are ca 50,000 K. These impact the gaseous species present, primarily N_2 and O_2 in an air carrier, to yield O-atoms and N-atoms and these in turn attack the pollutant molecules in a secondary process. Direct decomposition of pollutants by electron impact can occur but is much less probable at low pollutant concentrations.

The importance of this process as a pollutant removal process lies in its broad spectrum of reaction capability. Any compound, organic or inorganic, which can be oxidized by oxygen atoms is a potential candidate for removal by this process. In principle, any hydrocarbon could, with sufficient residence time in the SDP, be converted to CO_2 and water. In practice, reaction for one or two oxidation steps is sufficient to convert the pollutant to a product which is either much less undesirable or is more easily removed by some scrubbing process than is the original pollutant. This, combined with what we have found to be is a relatively low power consumption, raises the possibility of a broadly protective, always-on 'electric filter' for instant control of unexpected pollutant emissions. Clearly, the eventual application of SDP for pollution control will require a knowledge of its probable efficiency for various oxidations as well as prediction of probable reaction products from various classes of pollutants. For these reasons, we have investigated the basic reaction mechanisms of the SDP process as well as the practical operating parameters.

The possibility that ozone, which is concurrently produced by the attack of O-atoms on oxygen, is the secondary oxidizing agent is shown to be inconsistent with the kinetic data in the case of formaldehyde oxidation in an SDP.

Our investigation of the decomposition in SDP of a typical organic pollutant, benzene, shows products characteristic of attack by O-atoms (phenol) and N-atoms (nitrobenzene) and by direct electron impact on benzene (biphenyl), but the dominant product is phenol from oxygen atom insertion.

Similarly, we have found that the products of reacting HCN in an SDP using an air carrier are predominantly the insertion products HNCO and HOCN.

Extensive molecular orbital calculations have been undertaken in an effort to help map out the possible reaction pathways for oxidation of complex molecules such as benzene from which a large number of products have been obtained upon SDP oxidation. These calculations provide estimates of reaction enthalpies; from these the most energetically favored processes have been determined. Those of highest energy are predicted to be oxygen atom addition to the ring (23.2 kcal/mol) and subsequent ring opening to form a bi-radical (26.6 kcal/mol).

Experimental reaction parameters important to oxidation by SDP have been found to include voltage, residence time in the reaction zone, reactor geometry (wall area, width of discharge gap) and input power. All of these are inter-related so that the basic processes affected by each is still unclear.

Measurement of true minimum operating power is difficult since the coupled power is only that associated with the very short-lived microdischarges which occur randomly in time. Using both thermal balance methods and an integration of pulse power, it is estimated that the minimum energy requirements for single-step conversions is on the order of a few kilowatt-hr/kg of pollutant.

TREATMENT OF HAZARDOUS ORGANIC WASTES USING SILENT DISCHARGE PLASMAS*

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The conventional approach for the destruction of organic compounds is combustion. Although the generation of bond-cleaving free radicals is usually accomplished by thermal methods (i.e., high temperatures) or the photolysis of ozone or hydrogen peroxide, it can also be efficiently accomplished by non-thermal electrical discharge plasmas. Copious quantities of reactive free radicals can be produced in a gaseous waste stream by dissociating molecular oxygen with energetic electrons in a discharge. With some water present, the primary radicals are OH and $O(^3P)$. One promising technology for non-thermal plasma processing is based upon the "silent electrical discharge" that has proven to be industrially dependable for the generation of large quantities of ozone. Initial experimental and theoretical work on the use of these discharges for oxidation of SO_2 and NO_x in moist air and the destruction of selected hydrocarbons and halocarbons has been quite successful.

Silent discharge plasmas (SDP's) are commonly produced with near-atmospheric pressure (1-3 atm) electrical discharges. They are frequently called dielectric barrier discharges because of their characteristic means of production. Typically, one or both electrodes are covered with dielectric layers (e.g. glass) which separate them from the gas. The geometry is commonly either planar or cylindrical, where tubes rather than flat plates are used. This arrangement is an old one, first being employed by Siemens in 1857 for the production of ozone. Because of this use, it is frequently referred to as an ozonizer configuration. At gas pressures of order one atmosphere and gap spacings of order millimeters, a few localized intense arcs would develop in the gas between the metal electrodes without the dielectric. With a dielectric and the usual application of alternating high voltages (50 or 60 Hz power frequency to several kHz), substantial quantities of plasma are created by a large number of "microdischarges" in the gas, which are statistically spread in space and time over the electrode area. These microdischarges are transient discharges (usually thought of as streamers), fed by ionization and detachment and then arrested when charge build-up on the dielectric reduces the electric field in the streamer to the point where electron attachment dominates ionization and detachment. The overall development time for a microdischarge is quite short, for example, only a few nanoseconds for oxygen.

Because of the short duration of the microdischarges and the low ion mobilities, electrical energy in silent discharges is principally coupled into electron channels - electrons, ions, and the gas do not equilibrate - so the electrons are "hot", while the other species are "cold". Because the gas stays at near-ambient temperature, this process is also sometimes called "cold combustion". A very efficient transfer of electrical energy to electronic excitations of molecules and/or chemical processes in the plasma is realized by the SDP process. This property has been useful for over 100 years in the industrial production of ozone and, more recently, has been applied to the destruction of hazardous organic compounds. We are currently targeting solvents and volatile organic compounds (VOC's) which contain halogenated hydrocarbons for treatment using SDP.

At Los Alamos, SDP apparatus has been tested using a prepared gaseous feed containing the hazardous organic compounds trichloroethylene (TCE) and carbon tetrachloride (CCl_4). Typical apparatus operates at a gas flow rate of about 10 std liter/min and a power range of order 10 W to 1 kW. In representative experiments with a planar SDP reactor, we have removed TCE in the gaseous influent from 1,000 ppm concentrations to around 100 ppb in the gaseous effluent (CCl_4 appears to be more treatment-resistant). The measured figures of merit for the SDP reactor (electrical energy per mass of removed chemical) are 10's of kW-hr/g for » 99% removal of TCE and 100's of kW-hr/g for 90% removal of CCl_4, both being non-optimized cases in terms of waste concentration, carrier gas composition, water content, flow rate, and electrical power.

Upcoming experiments and field demonstrations will focus on lowering the final effluent levels and applying SDP technology on a practical industrial scale. In our Workshop presentation and paper, we will discuss experimental results, the results of our modeling efforts, and our plans for field demonstrations. A particular research concern is determining and preventing the production of intermediate and end-product chemical species that may be hazardous. We envision that the SDP process can eventually be developed to achieve hazardous compound reductions to levels of order 10 ppb or lower in gaseous waste streams.

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REMOVAL OF ORGANOPHOSPHONATE CHEMICAL AGENTS FROM AIR STREAMS*

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The rationale of this study was to learn with what efficiency it was possible to destroy chemical agents (more specifically, the simulants DMMP, DEMP, and O,S-DEMP) by interaction with discharged air products. Of particular interest to us were oxygen and nitrogen atoms, ozone, and $O_2(a^1\Delta_g)$, the lowest excited state of the oxygen molecule. In earlier work, Fraser and Sheinson [1] had concluded that reactivity of such materials with ozone was very low. We were able to demonstrate a variety of interesting phenomena but the most important lesson was the finding that surface effects play a dominant role in most of the work.

The atom experiments were conducted by introducing the organophosphonates (OGP's) downstream from a discharge in either O_2/Ar or N_2/Ar. Titration of the latter flow with NO converted the N-atoms to O-atoms, resulting in much reduced levels of O_2 or $O_2(a^1\Delta_g)$, compared to the oxygen discharge. For experiments with $O_2(a)$, combination of an O_2 afterglow with O-atom stripping by a mercury surface provided a clean source of $O_2(a)$. The concentrations of O and N-atoms were determined by standard titration techniques, whereas the concentrations of the OGP's and $O_2(a)$ were measured by VUV absorption and also mass spectrometry.

The importance of surface phenomena was quickly established by the observation that upon interaction with the discharge products, the OGP's were converted to a condensate on the flowtube walls. Analysis of the material for the case of DMMP + O-atoms showed that it was a mixture of 75% H_3PO_4 and 25% $H_2(CH_3)PO_4$. The presence of this material complicated the studies considerably, since it provided a medium for trapping the added OGP's, which then reacted both heterogeneously and homogeneously. The variable composition of the condensate also ensured that the monitored gas phase concentrations were unstable, and could vary slowly over periods of hours at fixed experimental conditions.

Interaction of the OGP's with O-atoms provided a dramatic visual effect - a white glow extended the length of the flowtube. Comparison of the spectrum of the emission with the glow from the O + NO reaction (for detector calibration) showed that the emitter was the PO_2 molecule, presumably originating with the O + PO reaction. This emission is known from other instances of O-atom interaction with phosphorous-containing molecules. The fact that the OGP's equilibrate with the wall condensate was clearly evident from the fact that the glow persisted for many minutes after the OGP flow was stopped.

Experiments were typically carried out with the OGP as the minority species, but a substantial excess of reactant was required, since it was soon established that up to twenty atoms or more of oxygen were consumed for every OGP molecule destroyed. Thus, the degradation products seem to be at least as reactive as the initial OGP. We note that complete oxidation of DMMP requires 10.5 atoms of oxygen.

Of the additives studied, O-atoms were found to be the most reactive. The OGP/atom reaction in an oxygen discharge flow presented some interesting phenomena, since we found that the atom loss for a given OGP level was greatly enhanced by O_2 itself, although O_2 showed no reactivity on its own. Our interpretation is that O_2 forms some intermediate product with partially degraded OGP's which reacts more rapidly with O-atoms than does DMMP. Similar behavior was observed when NO was substituted for O_2, although NO was much more effective than O_2 in this role; again, NO does not react directly with DMMP. In all cases, it is difficult to separate surface from gas phase effects.

A considerable range of reactivities of the three OGP's with O-atoms, N-atoms, and ozone was noted; the data we will present is analyzed as if homogeneous reactions were dominant, in which case the atom rate coefficients range from 10^{-15} to 10^{-12} cm^3s^{-1}. For ozone, the range is much smaller, 1-4 x 10^{-14} cm^3s^{-1}. The $O_2(a)$ molecule did not affect DMMP levels, yet DMMP was seen to quench $O_2(a)$, one molecule of DMMP quenching four $O_2(a)$ molecules. This behavior suggests that only physical quenching is involved.

Reactivity between DEMP and ozone was found to be extremely low at atmospheric pressure, in accord with previous estimates [1]. We believe that in low pressure flowtube experiments, ozone reactivity is strongly enhanced by surface reactions, and in fact, even at atmospheric pressure it was possible to greatly accelerate DMMP/O_3 interaction rates by coating surfaces with phosphoric acid. It is therefore possible that ozone can be an effective means for deactivating OGP's (or chemical agents) in a heterogeneous system.

*This work was sponsored by the Aeronautical Division at Wright-Patterson Air Force Base, OH.

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CONTROL OF GASEOUS POLLUTANTS AND AIR TOXICS BY SURFACE DISCHARGE INDUCED PLASMA CHEMICAL PROCESS (SPCP) AND PULSE CORONA INDUCED PLASMA CHEMICAL PROCESS (PPCP)

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Surface Discharge Induced Plasma Chemical Process (SPCP) and Pulse Corona Induced Plasma Chemical Process (PPCP) provide cost-effective means for the control of almost all of the gaseous pollutants and air toxics in a completely dry process. Although seemingly quite different, these two processes are based on essentially the same physical background - formation of highly nonequilibrium cold plasma in gas under ordinary temperature and pressure with the aid of nanosecond pulse discharges. Namely, the AC surface discharge of SPCP consists of a large number of small scale nanosecond pulse streamer discharges with ca. 10 ns risetime and 20-50 ns duration time, developing along the surface of an insulator plate to generate the plasma region in a thin restricted region of gas near the surface. Whereas the high-voltage nanosecond pulse streamer coronas of PPCP generates the plasma in the gas gap between the corona and counter electrodes. Both of them produce copious chemically active radicals of oxidizing or reducing nature, depending upon the carrier gas species, which either oxidize or reduce the gaseous pollutants and air toxics, such as NO, SO_2, Hg-vapour, trichloroethane, freons, toluen, etc.

The author and his co-workers developed novel Ceramic-Made SPCP-Units of both cylinder and plate types, both consisting of alumina ceramic layer (92% purity), corona electrodes out of tungsten attached on its surface and covered by high-purity alumina protection film (99% purity), and a film-like tungsten-made induction electrode embedded inside the alumina layer, facing to the corona electrodes with 0.5 mm gap. The unit is sintered in hydrogen furnace at 1,500 ^{0}C so that both electrodes become firmly fixed to the alumina layer with the aid of "metalized layers" in the alumina/tungsten interfaces. These particular SPCP-units have been widely used since more than 5 years, and proved their unique features in a very great chemical, mechanical, electrical and thermal strengths, as well as its compactness. There are two modes in the practical applications of SPCP: Direct Mode and Indirect Mode. In the Direct Mode the main stream of gas containing pollutants is passed directly near the plasma region of the SPCP-units, while, in the Indirect Mode, only the working gas (N_2, H_2, air, NH_3, etc.) is passed through the SPCP reactor to become activated, imparted copious radicals, and then fed into the main stream of gas containing pollutants. Both of them are very effective and useful, when properly designed, in particular in terms of working gas species and the residence time in the effective space of the reaction chamber.

The author also developed a nanosecond pulse power supply suitable to PPCP, using a rotary spark switch (Eldyne Pulser), and obtained very satisfactory results in control of various air toxics and gaseous pollutants in both laboratory and pilot plant tests. The risetime of the pulse voltage appearing at the corona electrodes is about 50 ns, depending upon the pulser, reactor, and feeder designs, and its half-tail about 200-500 ns, with the peak voltage 100-200 kV and pulse frequency 50-300 Hz.

In general SPCP is suitable to the applications of medium to smaller, and very small size, and those requiring stronger radicals possible to decompose more difficult gases (freon; trichloroethane). Whereas PPCP is suitable to the medium to larger and very large applications, where this process should be an integral part of gas cleaning system containing electrostatic precipitator or bag-house as well.

Detailed description of the hardwares for SPCP and PPCP are presented. Then, a number of test results for SPCP and PREP are described.

Finally, scientific and technical reviews of these two processes are presented, together with the future programme of development to make both of them to practical technologies.

APPLICATION OF CORONA TECHNOLOGY TO THE REDUCTION OF GREENHOUSE GASES AND OTHER GASEOUS POLLUTANTS

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To protect the environment, it has been of interest to clean exhaust gases and to reduce the emission of greenhouse gases. Non-equilibrium plasma can possibly be used to promote chemical reactions to reduce the emission of gaseous pollutants. One of the authors compared the efficiency of gas cleaning by electron beam irradiation, and by pulsed streamer corona discharge, using SO_2 as an indicator, and reported that the pulsed discharge could possibly be used for gas cleaning [1]. One of the authors have also developed the AC energized ferroelectric packed bed to promote chemical reactions [2]. In this bed, many pulsed discharges take place around each contact point of the ferroelectric pellets, and the discharge energy can be controlled by changing the dielectric constant of the pellet, and by the voltage waveform.

In order to reduce the emission of greenhouse gases (mainly CO_2), energy efficiency of the use of fossil fuel should be increased. Co-generation system has a possibility to increase the total efficiency to more than 80%. One of the most difficult problems to be solved for the system using diesel or gas engine, is the cleaning of exhaust gas, especially to reduce NO_x emission. Development of a compact deNO_x device will therefore contribute to expand the use of co-generation system in urban area, and to reduce CO_2 emission. In this paper, the experimental results on the reduction of NO_x, N_2O, CH_4, and CO_2 are reported.

(a) NO_x

(1) Utilization of pulsed streamer corona discharge generated by square-wave voltage: A wire-cylinder electrode (inner diameter: 20 mm) having an insulator on the inner surface of the cylinder, was used. Exhaust gas from a diesel engine with the NO_x of 450 ppm (NO = 40 ppm) was treated. The exhaust gas was cooled to room temperature, and introduced to the electrode system energized with a positive squarewave voltage of 20 kV amplitude, and 230 Hz frequency. During the overshooting period of the voltage, pulsed streamer discharges can be generated. NO_x decreased to less than 10 ppm at a treatment time of 0.56 sec, and less than 230 ppm (NO = 80 ppm) at 0.14 sec. It was found that the addition of ethylene enhanced the oxidization process of NO, and improved the removal efficiency of NO_x.

(2) Combination of plasma and catalyzer: A needle-mesh plate electrode with a separation of 40 mm was used. Catalyzer (20 mm thickness) was layered on the mesh electrode. Simulated flue gas with NO_x = 560 ppm (NO = 540 ppm), O_2= 10% and C_2H_4 =4000 ppm, was treated for 0.7 sec at a temperature of 240 C. With the square-voitage on, the NO_x decreased to 260 ppm (NO = 230 ppm), while without the voltage the NO_x remained at 400 ppm (NO = 370 ppm).

(3) Combination of plasma and liquid: A wire-cylinder electrode was used. A film of water was formed on the inner surface of the cylinder electrode. With a squarewave voltage of 17 kV and a treatment time of 6.9 sec, 920 ppm of NO_x (NO = 900 ppm) could be reduced to 260 ppm (NO = 150 ppm).

(b) N_2O

N_2O is generated in a fluidized bed coal combustion furnace. Test was made to reduce N_2O using the same apparatus as described in (a.1). Short pulsed voltage of 1 μs width and 120 Hz was applied. N_2O (1000 or 100 ppm) in nitrogen could be decomposed effectively with a removal efficiency of more than 80%. When O_2 = 1%, the efficiency decreased to about 30%. At the same time, peak value of the current pulse decreased sharply to 1/3 to 1/4 of that without O_2. With O_2 more than 2%, N_2O increased by about 20%.

(c) CH_4

The AC packed bed was used. CH_4 (2-5 %) diluted in Ar was treated. The treatment time was about 3 sec, and a 60 Hz AC voltage of 15 kV_{eff} was applied. About 10% of the CH_4 could be decomposed. It is noted that the decomposition of CH_4 by the pulsed streamer corona was not significant. When a mixture of CH_4 and H_2O (10%) was treated, formation of C_2H_2, C_2H_4 and C_2H_6 was observed. With a mixture of CH_4 and O_2, methanol and CO_2 were formed.

(d) CO_2

One of the authors brought the AC packed bed reactor to Prof. Chang at McMaster University, for a joint work, and carried out an experiment on the reduction of CO_2. The CO_2 concentration could be reduced by up to 18000 ppm, and 108 g of CO_2 could be reduced by 1 kWh of primary applied energy used in the packed bed reactor.

[1] A. Mizuno, J. S. Clements, and R. H. Davis, in *Conference Record of IEEE/IAS Annual Meeting*, pp. 1015-1020, 1984.
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DECOMPOSITION OF VOLATILE ORGANIC COMPOUNDS BY A PACKED BED REACTOR AND A PULSED CORONA PLASMA REACTOR

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Emissions of volatile organic compounds (VOCs) into the air is an increasing environmental concern. With the passage of the Clean Air Act, which requires increased levels of control for specific organics, the understanding and subsequent development of technologies for controlling these streams has been mandated. The conventional technologies for VOC control are carbon adsorption, catalytic oxidation, and thermal incineration. These technologies are widely accepted and well understood. However, with respect to some parameters, such as concentration and compounds treated, cost, and energy requirements, they have associated practical limitations. For these reasons, a novel technology was explored using an alternating current (AC) energized ferroelectric packed bed reactor and a nanosecond pulsed corona reactor as an alternative technical approach to control these pollutants at parts per million levels. This program was started in 1988 under a U.S. Environmental Protection Agency cooperative agreement and has also been supported by the US Navy.

Plasma Reactors and Experimental Systems: The pulsed corona reactor consisted of a wire-in-center geometry where the pulsed high voltage was applied, and a grounded stainless steel tube. The wire-to-cylinder distance was 11.5 mm, the effective wire length was 57 mm, and the wire diameter was 0.508 mm. The pulsed reactor employed a positive DC power supply that was altered to produce a short pulse with an extremely fast rise time (approximately 20 ns) through a rotating spark gap. A sharp-rise pulsed corona produces streamer corona which produces free electrons with only a limited number of ions.

The packed bed reactor employed a high-voltage AC power supply in conjunction with a tubular reactor packed with a high dielectric $BaTiO_3$ pellet layer. The pellets (1, 3, and 5 mm in diameter) were held within the tube arrangement by two metal mesh electrodes (2.5 cm separation). When external AC voltage (60 Hz) was applied across the high dielectric layer, the $BaTiO_3$ pellets were polarized, and an intense electric field was formed around each pellet contact point resulting in partial discharge. The reactor was filled with free electrons, as well as Ti and Ba ions which were observed by emission spectroscopy. These emissions may result from local heating near the contact point where the electron and ion bombardment and electron temperature are excessively high. Observation of the current waveform by an oscilloscope showed that the current consisted of the primary AC current and pulses with duration on the order of nanoseconds.

The dissociation/destruction efficiency of toluene, methylene chloride, and trichlorotrifluoroethane (CFC-113) at 50-1,000 ppm was evaluated. The effects of gas flow rate, concentration, reactor operating conditions, moisture content, and gas composition were investigated. Gas chromatography was used for analysis of reactant conversion for each VOC. The concentrations of CO, CO_2, O_3, NO, and NO_2 were measured at the same time. Each VOC was mixed into the gas stream before and after the reactor for better understanding the destruction mechanisms.

Results and Discussion: Complete destruction was obtained for toluene using both reactors. The conversions of methylene chloride at 95% and CFC-113 at 67% were achieved for the pulsed corona reactor and somewhat lower destructions for the packed bed reactor. Addition of moisture reduced the VOC destruction efficiency as well as ozone production by 10%.

For the packed bed reactor, the corona onset voltage decreases as the pellet diameter increases. Correspondingly, the sparking voltage increases with decreasing pellet diameter. The destruction starts to take place above the corona onset voltage, and conversion efficiency increases with increasing effective AC voltage. The destruction efficiency increased with decreasing pellet size, increasing the residence time, and decreasing concentration. Toluene mostly decomposed into CO_2, H_2O, and CO. The CO concentration reached 700 ppm near the sparking for all pellet sizes although CO concentration was proportionally lower for lower toluene concentrations. When the pellets were replaced with 3 mm diameter glass spheres (dielectric constant of 4), pulsed waveforms were no longer observed, resulting in no destruction. This implies that the molecular decomposition is strongly associated with electron activity.

The pulsed corona reactor has been proven to destroy compounds in different destruction mechanisms. Toluene destruction achieved was essentially the same when it was mixed into the gas stream before and after the reactor for both O_2 and zero air, but no destruction occurred for N_2. The data when the toluene is fed in approximately 5 s downstream of the reactor also yields very similar destruction. Apparently the reactive species causing the destruction is a long-lived species of oxygen. Note that a brownish-yellow residue (high molecular-weight compound) was observed on the reactor electrodes for toluene but no residues for other VOCs.

The methylene chloride post-reactor testing showed that destruction was possible in this configuration. The through-the-reactor gases tried were zero air, oxygen, nitrogen, and humidified zero air. Destruction was achieved downstream of the reactor for all of the inlet streams containing oxygen. Inlet nitrogen produced no destruction. The dry zero air produced better destruction than the humidified zero air, but the pure oxygen stream produced the best results with destruction similar to that when the VOC containing stream went through the reactor. NO and NO_2 outlet concentrations for these runs never exceeded 3 ppm. These data show that the mechanism(s) producing the methylene chloride destruction and the mechanism(s) for toluene destruction are not identical. Toluene is destroyed equally well through and after the reactor with no noticeable increase when pure oxygen is run through the reactor; whereas, methylene chloride is not destroyed as well after the reactor and shows a definite improvement when pure oxygen is used. This indicates that the mechanism that destroys the toluene is either less dependent on direct contact with electrons or on the short lived species. Methylene chloride destruction appears to have a strong dependence on the presence of oxygen. Neither VOC is destroyed using pure nitrogen through the reactor indicating that no long lived nitrogen species is involved in the destruction process.

CFC-113 could not be completely destroyed and appears to be volumetrically limited in its destruction ability. That is, a certain fraction of the CFC-113 is in a part of the reactor where it will not be destroyed, regardless of the voltage of the power supply or the concentration of the

CFC-113. This indicates that CFC-113 is destroyed either by direct electron impact or by a very short lived product.

Not only can the plasma technology be used to decompose a variety of compounds, but also the relationships of concentration and residence time to destruction show that increased destruction levels can be achieved with increasing residence time and lowering concentration. Therefore, this process can be applied to many practical situations.

REACTION KINETICS FOR FLUE GAS TREATMENT OF NO_x

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During the past several years, control of NO_x emissions has become a national issue. NO_x emissions are a leading contributor to acid rain as well as contributing strongly to photochemical smog. Current state-of-the-art technologies have essentially reached their maximum potential. To overcome these problems, advanced processes have been developed utilizing plasmas that generate large numbers of various radical species that promote the removal of NO_x. Considerable research has been conducted on e-beam and laser generated plasmas. However, low energy efficiencies associated with generation of the high energy plasmas has kept these processes from moving rapidly into commercial operation. Recognizing the benefits of the advanced high energy techniques, a new process based on the generation of a low energy plasma, a soft corona discharge has been developed that has demonstrated NO_x emission control approaching 99% reduction. The process is an electro-catalytic process in which the electrons generated by the soft distributed corona discharge promote the dissociation of the NO_x molecules. The performance of the current state-of-the-art systems is dependent upon the oxygen level in the flue gas. This is not the case for this process. NO_x reduction with this process is relatively insensitive to oxygen level. Greater than 90% reduction is maintained with flue gas oxygen levels ranging from 2 to 15%. Cost estimates for this technology achieving 96% reduction are slightly less that of an SCR system achieving only 90%. This paper discusses the data and provides a mechanism for the chemical kinetics occurring in the system. It also presents preliminary cost data compared with the current state-of-the-art technologies.

PULSED CORONA PROCESSING

MODELING OF PLASMA CATALYTIC REDUCTION OF NO_x AND SO_2 IN FLUE GASES

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The growing concern about the quality of the environment has led many Research Laboratories and Electricity Boards to devote more and more attention to new technologies for the removal of polluting agents from industrial flue gases, namely the fly ash and the acid rain precursors NO_x and SO_2.

The Italian program on "Flue Gas Clean-up" has devoted a significant effort to test and develop new electrostatic techniques for reducing the pollutant effluent concentrations within the permissible limits proposed by the Commission of the European Communities.

In particular a Plasma Catalytic Process has been developed for simultaneous NO_x and SO_2 removal by means of impulse corona energization of the flue gas. With this technique ions and oxidizing radicals (O, OH, OH_2, etc.) are produced in the flue gas: the reactions of NO_x and SO_2 with radicals form several acids that can then be neutralized by injecting in the gas ammonia or lime; the final product can be removed from the flue gas in an electrostatic precipitator.

In the present paper this technique is briefly described, and the simulation models developed in order to understand the basic plasma processes and to guide the engineering development are described.

The simulation of the corona discharge has been carried out in subsequent steps, which can be differently combined, depending on the specific application:

1) the calculation of the transport coefficients in the flue gas mixture, on the basis of the electron collision cross sections in the parent gas;

2) the field calculation, either under Laplacian or Poisson's conditions, optimized for the typical reaction chamber geometries;

3) the impulse corona simulation, in which the development and propagation of the corona streamers is analyzed and the production of primary ions and radicals within the gap is computed.

The results of the streamer simulation make it possible to calculate the distributions of the active species (positive and negative ions, excited molecules, and radicals) along the branches of the impulse corona.

As the streamer filaments follow the geometric lines, the structure of these branches depends on the geometry of the plasma reactor (wire-cylinder, wires between planes, etc.). In any case the initial distribution of the active species is strongly non-uniform within the reactor volume.

The non-uniformity of the impulse corona structure will disappear in some milliseconds because of diffusion processes and turbulent gas mixing.

The plasma chemical reactions occur therefore in two different conditions:

- the fast reactions (ion and radical conversion) will occur on a fast time scale, typically some tens of microseconds, within the corona filaments with high density of the active species;

- the slow reactions (chemical catalysis) will occur on a much longer time scale, typically some seconds, in the homogeneous gas phase with the average densities obtained after the gas mixing.

In the present paper the fast conversion reactions (which are almost the same for any plasma catalytic reactor) are analyzed in detail and the results of a kinetic computer model are presented.

Furthermore, the slow catalytic reactions are discussed for two different applications actually under development:

- the simultaneous reduction of nitrogen and sulfur oxides (NO_x and SO_2) in combustion flue gases;
- the "cold combustion" of volatile organic compounds (VOC) in the ventilation air of industrial installations using organic solvents.

EXPERIMENTAL STUDIES ON NO REMOVAL INITIATED BY NANOSECOND CORONA FROM METHANE COMBUSTION PRODUCTS

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The extensive research on simultaneous removal of SO_2, NO_x and dust with pulsed corona is still under development [1-3]. The measurements presented are part of a program to investigate the streamer corona characteristics and production efficiency of the active radicals in real flue gas.

To investigate the NO removal effect of nanosecond corona discharge energization of flue gas, a slipstream test rig was designed and installed near vapor generator burning methane. The temperature and flue gas rate were regulated by two sliding damping. The nominal flue gas conditions were gas flow rate of 7 - 31 Nm^3/h, gas temperature of 80 - 200 C, NO initial concentration of 50-200 ppm, 19% H_2O, 0.5% O_2, 9.5% CO_2, and 71% N_2. Oxygen could be injected in the flue gas upstream of the concentric cylinder discharge chamber. The wire discharge electrode had a diameter of 1.5 mm and the cylinder electrode had a diameter of 20 cm. A special wide-range Rogowski-type coil and capacitor divider were designed to measure voltage and current at the inlet of the discharge reactor. The pulse voltage had a peak value ±65 kV, 50 ns risetime (~ 1 kV/ns), 200 ns pulsewidth (FWHM). The pulse repetition frequency was regulated up to f = 1100 Hz.

The maximum energy dissipated in the discharge chamber per impulse was 0.3 J (f = 100 Hz). The maximum average dissipated power was 260 W (f = 1100 Hz). The largest part of energy was introduced in volume within initial 100 ns. The input specific energy ranged from 0.5 to 24 Wh/Nm^3. The length of wire electrode was 3 m, that is why the time of electromagnetic pulse propagation was 10 ns. At high dV/dt the pulses proceed in the reactor in the form of traveling waves with attenuation due to corona. This leads to complicated electromagnetic process in the reactor that is electric load with distributed parameters. Fig. 1 shows a typical waveform of current at two temperatures of gas stream. The current is larger in a positive corona than in a negative one.

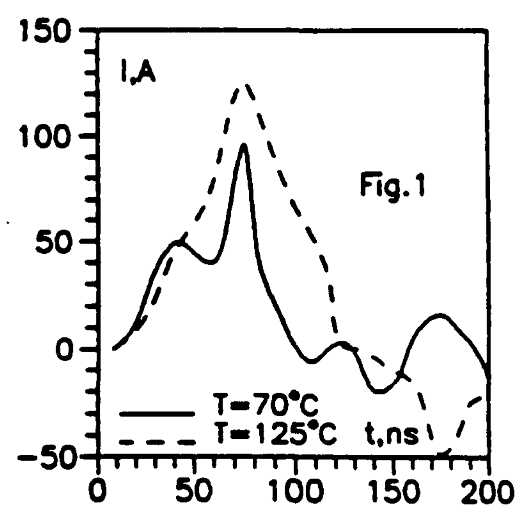
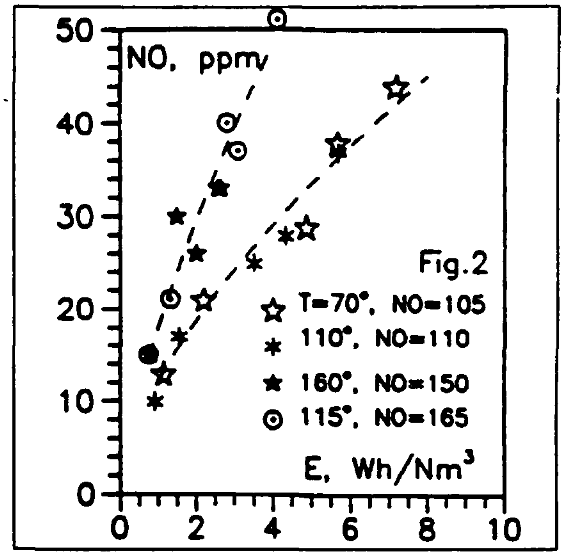


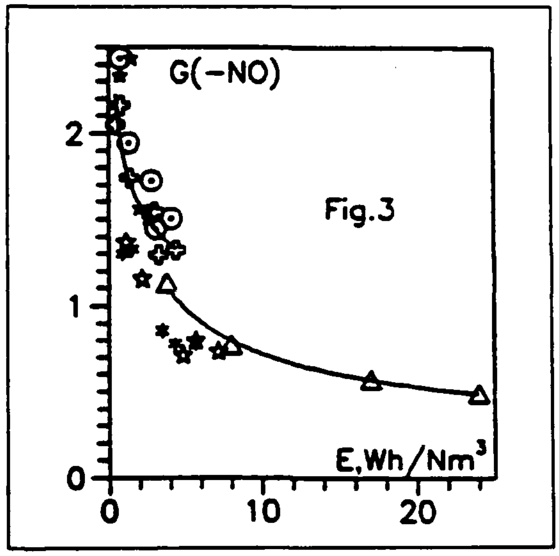
Fig.1

There are reasons to believe from the corona capacitance model [4] that the streamer radius propagation was less than 5 cm. It was found that convection of the gas was created [5], which makes possible the production of active radicals in the full gas stream. The amount of removed NO depends on the energy transferred to the gas with the nanosecond corona process, as can be seen from Fig. 2. It is clearly shown in Fig. 2 that there is a nonlinear correlation between the energy and the removed NO. There is a good agreement for experimental data represented in Fig. 2 with identical initial NO concentrations and pulse voltage amplitude when the temperature is changed from 70 °C to 160 °C. The removed NO was found to increase with increasing initial concentration of NO up to 150 ppm.

The removal efficiency was not more than 0.6 when the energy transferred to the gas was less than 10 Wh/Nm^3. The degree of NO removal depend slightly on initial NO concentration. With an initial NO concentration of 90 ppm, 95% was removed at a specific energy of 20 Wh/Nm^3 when gas flow rate was 7.3 Nm^3/h (gas residence time was 46 s). The efficiency of the discharge is represented by the number of NO molecules removed per 100 eV of energy absorbed (G value). The dependence of G on the energy transferred into the gas is shown in Fig. 3. Although the energy absorbed per impulse in the gas was larger for positive polarity the plasma-chemical efficiency of negative and positive pulses are the same. The value of G measured in this work is less than that measured in [1,2]. There are reasons to believe that this fact is explained by lower oxygen concentration in these experiments.

The results obtained are of interest to the creation of technology for the abatement of NO_x from flue gas without much oxygen concentration.





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PULSED CORONAL DISCHARGE FOR COMBINED REMOVAL OF SO_2, NO_x AND FLY ASH FROM FLUE GAS*

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The efficient removal of NO_x, SO_2 and fly ash from flue gas is essential for the optimum use of coal for power generation. We are exploring the use of pulsed corona in the removal of these pollutants. Our approach utilizes metal electrodes with a peak to average field above 6.

The principal experimental apparatus utilized by this effort uses a closed loop gas system. This system permits the introduction of various gas combinations prior to testing. Analysis can be conducted during or after these tests. This processor can accommodate electrode geometries up to two inches in diameter. The recirculated gas can be heated to up to 400 degrees Fahrenheit. Heating is important to determine the effect on electrical discharges, chemical reactions and water content.

The processing chamber has been designed with an outer pipe of two inches in diameter. This tube can be used as an electrode; other geometries of smaller dimensions can be placed inside. The current reaction chamber is six inches in length, but can be increased as needed to match the impedance of the cable to that of the processor for maximum energy transfer. Configurations tested for NO removal are a 0.060 inch stainless wire in a 1.6 inch stainless tube, a 0.040 inch platinum wire in 1 inch tube lined with 0.001 inch platinum foil, and a center conductor of 0.5 inch diameter thin brass discs spaced at 0.25 inches in a 2 inch stainless tube.

We have changed the charging circuit to allow high pulse rates. The present system performs well up to 20 pulses per second. Most of the data taken has been at a pulse rate of 5 pps. Part of the reason for this rate is that we want mixing to take place between pulses. The volume of the reaction chamber is approximately 0.3 liters and the flow rate is from 3 to 5 liters/second. Once an optimum geometry is found we will determine the efficiency of single pass processing. This will include reducing the flow to be just in turbulent flow and then increasing the pulse rate.

The performance of the removal in ev/NO molecule is a function of the NO concentration. We are presently charging the system to approximately 600 ppmv. NO reacts with itself in the presence of air and the change in concentration is proportional to the square of the concentration. This means that the natural rate of NO reduction at 500 ppmv is 25 times that at 100 ppmv. This effect must be subtracted from the reduction due to pulsed plasma processing. The natural reduction of NO has a negative temperature coefficient, which means the reduction is less at higher temperatures. At room temperature the natural decay at 500 ppmv is approximately equivalent to twenty pulses per second pulsed plasma processing. We feel the present system gives good data to the 500 ppmv level and can go to higher ppmv at higher temperatures.

Measurement of efficiency is determined by measuring the current and voltage as a function of time. The integral of the V*I product is calculated during the pulse which gives the energy per pulse. This value times the pulse rate gives the total energy per unit time. Knowledge of the volume and the reduction of NO gives the efficiency of removal. This is calculated in electron volts per NO molecule.

Breakdown after the onset of coronal discharge can occur but is a function of the stress and pulse length. We have constructed a new processor this year that can accommodate many electrode shapes at temperatures up to 400 degrees Fahrenheit.

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HYDROGEN SULFIDE DECOMPOSITION BY MEANS OF PULSED CORONA DISCHARGE*

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Hydrogen and fuel gas systems often contain hydrogen sulfide as an impurity, especially when derived from coal gasification. Hydrogen sulfide is usually present in concentrations up to a few percent by volume. The commercial use of such a gas calls for its desulfurization to the levels of .1 ppm (fuel cells) to 10 ppm (SNG).

The methods generally used for the desulfurization of these gases are liquid absorption of H_2S by an alkanolamine solution or a sodium carbonate solution, liquid phase oxidation of H_2S to sulfur by means of dissolved oxygen carriers such as sodium vanadate, and dry oxidation of H_2S by iron oxide. Except for the iron oxide process, these methods require several steps for regeneration of the absorption liquor and for sulfur production. The iron oxide process is no longer economic due to the need to replace and dispose of spent oxide.

Some recent experimental studies lead to the conclusion that H_2S decomposition to hydrogen and sulfur can be directly achieved electronically, without the introduction of chemical sorbents. The chemical kinetics of gas phase electronic H_2S decomposition is well understood. Initially, hydrogen ions and atoms are created through H_2 collisions with energetic electrons, and the H atoms are active in the conversion of hydrogen sulfide to elemental sulfur according to the reactions:

$$H + H_2S \rightarrow H_2 + HS$$
$$H + SH \rightarrow H_2 + S$$

The energetic electrons needed to initiate the reactions cited above can be generated by many available technologies. Minimum required electron energy is the ionization potential of hydrogen, which can be achieved in gas discharges such as glow or arc. Alternately, high energy electron beams can be employed in which each primary electron of energy on the order of one MeV produces thousands of hydrogen ions.

Experiments in H_2S dissociation have been carried out utilizing many of these sources of energetic electrons. While the work done to date shows promise, many questions remain unanswered. Most of the experiments have been done at or below atmospheric pressure. In order to determine if this electronic method has real-world applicability, high pressure performance must be demonstrated. Few of the experimental investigations explicitly documents the energy efficiency of the electrical discharge promoted molecular conversion. Electric discharge chemistry tends to be energy intensive, especially at high pressure, hence it is necessary to determine the energy efficiency of the process in order to estimate commercial viability.

This paper describes the results of the use of a wire-in-tube corona reactor, energized by short voltage spikes, to decompose small concentrations of hydrogen sulfide contained in hydrogen. Parameters investigated include the reactor geometry, hydrogen sulfide concentration, corona power, and the nature of the product. A mathematical model is formulated which accurately predicts experimental results, and a commercial scale design is proposed.

*This work was performed at the Research Cottrell Air Pollution Laboratory under the auspices of the Gas Research Institute under Contract Number 5087-222-1482.

LABORATORY STUDIES OF PLASMOCHEMICAL OXIDATION PROCESS ENERGIZED BY PULSED STREAMER DISCHARGES

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Oxidation processes energized by pulsed corona and barrier discharges have been studied experimentally.

1. SO_2 oxidation in air by corona discharge. Peak voltage amounted to 50 kV, repetition rate was up to 1 kHz, pulse duration 100-500 ns. SO_2 concentration was measured using infrared and chemical methods. The gas power input was varied by frequency, peak current, and the time of action. The water vapour concentration varied up to 30% vol. The energy cost of the process was about 15 eV/molec. The higher energy cost was obtained for the case of water-lacking system. The stable energy cost of the process in a wide range of discharge and gas parameters proves the unchained SO_2 oxidation under our conditions. H_2S oxidation in air was studied in this discharge system. H_2S concentration was measured by UV technique. The energy cost of the process was approximately 70 eV/molec.

2.Pulsed barrier discharge was made in order to increase the electron temperature. Pulse duration in this system is 100 ns. For 2 mm gas gap the peak voltige was 25 kV. In such sistem the energy cost of the process was 15 eV/molec. H_2S, but only in presence of the liquid water. In presence of the vapour the energy cost of the process was approximately 90 eV/molec. H_2S. The concentration of the vapour water did not affect the experimental results up to appeariance of liquid water. H_2S oxidation in CH_4 and H_2 was studied in this system as well as CS_2 and mercoptans oxidation in air. The results are given in the table:

Main Gas	Pollutions 0.1-1%	Products	Energy Cost eV/molec	Purification Degree
CH_4*	H_2S	H_2SO_4	30	>99%
Air	H_2S, CS_2, SO_2, mercoptans	H_2SO_4	15	>99%
H_2	H_2S	S	15	>99%

The models of chemical process are discussed. On the basis of these experiments we are constructing a pilot plant for purification in the paper industry air from H_2S and mercoptans with an averege power of 20 kW.

* -additional input of oxygen with concentration near [H_2S]

FUNDAMENTALS

EMISSION SPECTROSCOPY OF CORONA DISCHARGES

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In gas treatment by electrical discharges with the aim of converting harmful gas components to substances which can either be readily precipitated or are considered innocuous one can follow the later reaction sequences by conventional chemical kinetics analysis. However, this requires an input of initial conditions which are largely determined by excited states and radicals directly or indirectly formed in the discharge itself. Some of these early reactions can manifest themselves in the emission of radiation from the discharge in the fairly accessible spectral range from 190 to 850 nm. Using a short-duration stimulus one can obtain the time dependence of emission and thus gain access to certain reaction rates.

In contrast to the time-honoured and generally very useful conventional discharge flow technique where one obtains reaction rates by means of converting a time dependence to a spatial dependence of reactant and/or reaction product concentration, the measurement of time dependent emission of radiation can be useful over a very wide range of partial and total gas densities up to atmospheric or beyond as long as one can obtain an adequate stimulus short enough in comparison to the actual reaction time constants. Although some information can be obtained from the emission from a glow corona which can be operated readily at nearly all gas densities, a Trichel pulse corona offers a regularly repetitive short-duration stimulus useful for determination of reaction rates and/or reaction origins. To generate a Trichel pulse corona one requires fairly concentrated negative ion formation. This sets a lower limit on gas density ($\approx 10^{18}$ cm^{-3}) and demands a gas which is at least weakly electronegative - for example, 0.1% of oxygen in Ar + N_2 can produce a respectable Trichel pulse discharge. Sometimes the Trichel pulse regime can be extended to lower partial densities of the gas of interest by addition of a buffer gas (e.g. Ar for H_2O) so that excited state decay can still be investigated under these conditions though the gas on its own would not produce a Trichel pulse discharge. Comparison measurements utilizing an externally-pulsed positive corona are envisaged.

The time-integrated emission spectra will give some limited information on gas composition and luminescent reactions. Time-gating the detection circuits can immediately furnish further information as to which emissions originate from direct excitation by electrons (of gas constituents originally present) and which are caused by subsequent reactions of primary discharge products. Once the reactions are identified, the time dependence of particular emissions can be recorded to obtain the time dependence of the density of the associated excited states. A highly sensitive and very suitable method for this is time-correlated single photon counting as used in fluorescence analysis.

In connection with flue gas treatment by discharges the formation of radicals reacting with nitrogen oxides and the balance of these oxides are of particular interest. The hydroxyl radical OH which is here considered very important because of its reactions with NO_2, SO_2 and NH_3 manifests itself (at least in its A state) by OH(A-X) emission which decays rapidly (some 10^{-8} s) indicating a fast depletion of OH(A). Direct excitation of NO produces NO_γ emission, while the dominant emission from N_20 is NO_β which is, however, indirectly formed: This manifests itself in a slow rise of the emission which continues well after the peak of the corona current pulse. From the light pulse shape, one can determine rough values of the formation and destruction rate constants for NO(B). For such evaluation of reaction rates, it is useful to have the time dependence of the electron density in the active discharge region. For the example mentioned, one can make use of the emission from $N_2O^+(^2\Sigma)$ which is evidently directly excited in electron collisions and has a very short lifetime so that this emission remains available for diagnostics even in gas mixtures containing a high percentage of water vapour besides N_2O. In gas mixtures containing N_2 (like standard flue gas) the emissions originating from $N_2(C)$ can serve for recording the time dependence of electron density.

Our attempts to clarify the process of NO(B) formation from N_2O (precursor $N(^2D)$ or $O(^1S)$) by way of detecting ArO^* excimer emission [1] have so far failed to give evidence of the presence of $O(^1s)$.

To support efforts to simulate discharges in flue gas, measurements of effective ionisation rate coefficients and electron drift velocities have been made for a typical flue gas composition, using the conventional PT method. Though it would be desirable to obtain excitation rate coefficients etc. also at given constant values of reduced field strength E/n instead of the wide range of E/n encountered in any corona discharge, such measurements present severe problems of intensity, filtering and imaging and have thus - for the time being - not been further pursued.

Systematic studies of specific emissions from corona discharges are being expanded and should in time contribute further to surveying and elucidating the early processes in discharge treatment of polluting gases and are also contributing to provision of quantitative rate information much of which is so far scarce for situations in which electronically excited states are as important as they are in discharges.

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ELECTRICAL AND OPTICAL INVESTIGATION OF PULSED STREAMER CORONA*

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In several experimental investigations the effective removal of pollutants like NO_x and SO_2 from flue gas by streamer corona discharges has been demonstrated. The optimum pulse conditions for production of streamer corona are not well known. The objective of this experimental study is to get insight on the influence of pulse parameters on the formation and propagation of streamers and their energy dissipation.

The discharge is produced in a wire-plate geometry (wire length = 50 mm, wire radius = 0.3 mm, gap distance = 35 mm) in which a flow of dry air is maintained. The standard pulse conditions are: repetition frequency f = 20 Hz, peak voltage V_p = 25 kV, rise time t_r = 40 ns, decay time = 500 μs. The discharge structure is studied by using a two-dimensional CCD-camera. The measurement of local light emission at different positions (using quartz fibers coupled to a fast photomultiplier) is used to determine the inception voltage of individual streamers, the ignition delay time of a streamer with respect to the moment of the first streamer being formed, and the streamer velocity. Averaged values and their statistical variation are obtained from at least 100 measurements during repetitive operation of the discharge.

In Figure 1 the discharge structure is given for standard conditions. The emission from a cylindrical volume, with a diameter of 1 mm, has a duration of less than 10 ns. Thus the observed profiles are related to light emitted by the streamer front only. The streamer number density increases when the voltage is increased (4-5 streamers per cm at 25 kV and 6-7 streamers

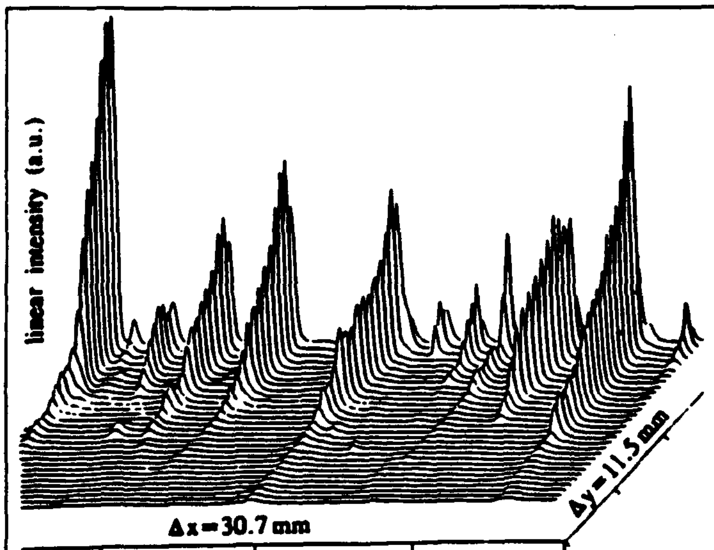

Fig. 1: CCD-picture of positive streamer corona.

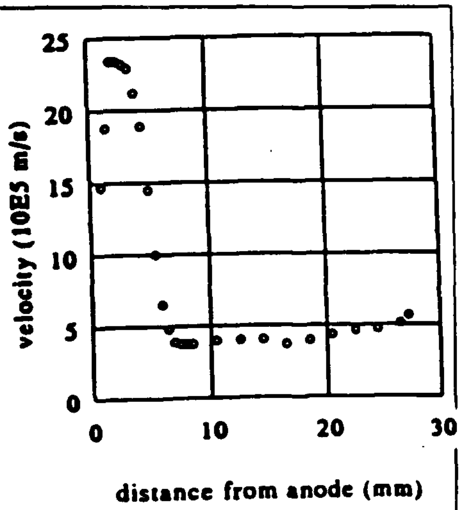

Fig. 2: Streamer velocity.

per cm at 35 kV) or when the rise time is made shorter. At voltages above 35 kV the light emission of individual streamers decreases. This may be due to the increasing interaction of streamers when their number density or space charge field increase, or when their inception delay time becomes smaller.

Streamers with intense and weak emission are observed. For the intense streamers a transition from high to low emission is present at 3-7 mm from the anode. This distance is greater than the outer radius of the critical volume (2 mm for standard conditions) and it increases with voltage. The observed streamer diameter (full width at the 10% value of the intensity maximum) is about 750 μm. However, this value is an overestimation of the real diameter because of the limited depth of field and the cross sensitivity of the CCD-camera pixels.

The streamer velocity (Figure 2) first increases to a maximum of 23×10^5 m/s. At the "transition radius", observed from the CCD-pictures, the streamer velocity falls down to 4×10^5 m/s. The velocity increases slightly when the streamer approaches the cathode. This may be due to the release of photoelectrons at the cathode.

The table gives the energy per pulse per meter wire (E in mJ/m) and the average inception voltage (V_i in kV) as a function of pulse parameters.

t_r=40 ns f=20 Hz		t_r=40 ns V_p=25 kV		V_p=25 kV f=20 Hz			V_p=30 kV f=20 Hz		
V_p	E	f (Hz)	E	t_r (ns)	V_i	E	t_r (ns)	V_i	E
25 kV	110	1	110	40	24.4	110	40	28.6	263
35 kV	800	100	95	130	22.8	96	130	25.5	168
40 kV	1200	1000	60	250	21.1	78	250	23.1	125

When changing the discharge frequency the ratio of the gas residence time and pulse period is kept constant. The breakdown probability becomes non-zero for $V_p > 30$ kV. Breakdown is avoided by switching the pulse off after 400 ns. The current is then almost zero. A DC-bias up to 12 kV (keeping V_p constant) has no influence on the dissipated energy per pulse, even at the frequency of 1000 Hz. For $V_{DC} > 12$ kV (the DC-corona onset voltage), the energy per pulse decreases.

At $V_p = 25$ kV the inception voltage is in the range 21-25 kV with 90% probability. The influence of rise time on the energy dissipation per pulse can be ascribed to the inception voltage. Its averaged value is less dependent on rise time when $V_p = 25$ kV than when $V_p = 30$ kV.

The ignition delay time between individual streamers is always less than 20 ns even when, at lower voltage (for example 20 kV), the streamer inception time becomes of the order of 1 μs with large statistical variations. So under all pulse conditions the streamers are formed simultaneously.

Interaction between adjacent streamers is demonstrated by the CCD-pictures and the ignition delay time measurement. Two regions with different streamer emission and streamer velocity are clearly observed. The main parameter determining the energy dissipation is the inception voltage. The decrease of energy dissipation per pulse, when the repetition frequency is increased, is usually attributed to space charge accumulation between the pulses. However, the fact that the energy dissipation is independent of DC-bias, which can remove space charge in between the pulses, does not support this explanation.

*This work is performed with support from the European Community, NV KEMA, and the Dutch Foundation for Applied Research (STW).

MEASUREMENTS OF SPACE CHARGE DENSITY PRODUCED BY AN ENVIRONMENTAL IONIZER

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An environmental ionizer is a device widely used to produce ionization in the ambient air and to reduce contamination levels in clean rooms. In the present work the corona discharge produced by a commercial ionizer consisting of a pair of point electrodes, both at a negative voltage of -6 kV, is characterized to estimate the space charge density in the air at various distances from the ionizer.

The measurements were made by using the principle of biased probe originally described by Tassicker [1]. The probe system consists of a circular plane probe of radius r_p, located complanarly and coaxially within a circular ring of radius r_a so that an annular gap of width $g = r_a - r_p$ is thus formed. A bias voltage is applied between the two parts to control the conduction current to the probe. From the current-voltage characteristic of the probe the magnitude of the external electric field at the probe surface can be deduced. The estimation of the space charge density can be made from the combined current density and field data, assuming the mobility of the charge carriers is known. The applicability of this probe technique was demonstrated by Selim and Waters [2].

We have obtained values of negatively charged particles density varying from 12×10^{13} m^{-3} at a distance of 3.5 cm from the ionizer (in the central axis between the twin-point electrodes) to 0.6×10^{13} m^{-3} at a distance of 30 cm. Additional analysis in a point-plane corona in air was also performed and comparisons are made with previous work. The results have shown that the biased probe is a valuable diagnostic tool to determine the properties of discharges in air such as those produced by environmental ionizers.

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EFFECT OF VIBRATIONALLY-EXCITED STATES AND METASTABLES ON DISCHARGE CHARACTERISTICS

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Modeling of electrical discharges for pollution control requires a lot of sophistication due to the high non-equilibrium character of these discharges. The model should couple plasma physics and plasma chemistry in a self-consistent way in order to describe both the electronic component and the different chemical radicals acting in the discharge. The plasma chemistry is usually simplified by neglecting the presence of excited states which, however, could take an important role in affecting chemical reactions and the energy distribution of free electrons. These effects have been discussed by our group in these last years for low pressure-long residence time discharges. In this lecture we will present results for high pressure-small residence time discharges. Our aim is to show the importance of vibrational and electronic states of molecules in affecting the dissociation and ionization processes, as well as the electron energy distribution function. Our model is based on a self-consistent solution of the Boltzmann equation coupled to the vibrational and electronic master equations as well as with the dissociation kinetics. It includes each vibrational level of the ground state of the diatomic molecule as a true chemical species with its own electronic cross sections. Although we consider nitrogen plasmas, our results can be extended to more realistic air mixtures containing different pollutants. We consider different non-equilibrium situations created by a temporal superimposition of typical E/N and electron density values followed by relaxation periods.

THEORY OF PULSED CORONA IN AIR AND FLUE-GAS MIXTURES

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A theoretical examination is made of the mechanism of corona formation in air and flue-gas mixtures at 100 kPa. The evolution of positive ion, negative ion, and electron densities is described by one-dimensional continuity equations, with space-charge electric fields determined by the disc method. The effects of ionization, attachment, recombination, electron diffusion, and photoionization are all included. The numerical method used [1] allows resolution of the streamer head with a mesh spacing of 1 μm. The impulse voltages applied have rise-times of 15-50 ns and peak voltages of 50-100 kV. Seed electrons are released 1 ns after the start of the voltage rise. For a 0.5 cm diameter positive sphere located 6.5 cm from a negative plane, the calculated circuit current rises abruptly to form a corona onset current pulse followed by a subsequent pulse. However, when compared with similar pulses computed [1] for SF_6, the rise-time and the width of the current pulses are much larger for air and flue-gas mixtures, so pulses are less distinct than found for SF_6. The reason for the wider, more slowly rising pulses is that in air and flue-gas mixtures the streamers propagate more slowly than in SF_6, thus their movement is more comparable with the voltage rise time. Once the voltage reaches a maximum the circuit current falls rapidly, but not as fast as in SF_6 [1]. During the current rise for both air and the flue-gas mixtures a streamer moves out into the gap along a 100 μm channel, with the electric field in the streamer trail $E \geq E^*$, where $E^* \approx 30$ kV/cm is the field where ionization equals attachment. According to the criterion for the limits over which this field may vary [2], the field in the streamer trail is not as strictly clamped close to the value E^* in this case as it was in SF_6. For a peak voltage of 50 kV, the streamer propagates ≈ 2 cm into the gap for both air and a typical flue-gas mixture [3], with little difference in the streamer characteristics. The main difference is that the streamer propagates ≈ 5% less in the flue-gas chosen [Ref. 3 'esp2'], due to the slightly higher value of attachment at high values of E/N, where N is the neutral gas density.

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MULTI-DIMENSIONAL MODELING OF THE DYNAMIC MORPHOLOGY OF STREAMER CORONAS*

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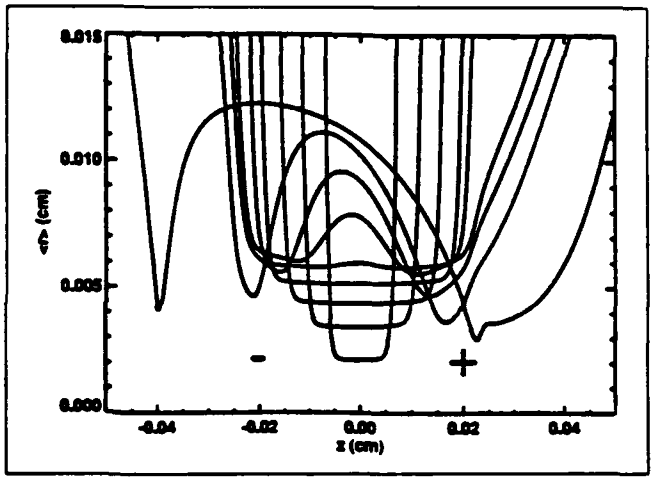
There is currently an increasing interest in streamer coronas because of their application to pollution control devices. In these devices, the streamers produce energetic electrons which, through dissociation and ionization processes, generate active radicals that in turn react with the toxic molecules. The morphology of streamer coronas determines in large part the energy distribution of the electrons produced in these devices. Within the short lifetime of the streamers, the ions do not experience significant movement and therefore do not contribute to the power consumption. Because of the complexity of the equations describing streamer dynamics, most of the simulations have been restricted to one (longitudinal) (1-D) spatial dimension. Some low-resolution two-dimensional simulations have been performed, but so far have been restricted to plane-parallel electrode configurations. We have developed two-dimensional (2-D) and three-dimensional (3-D) streamer models that can be applied to arbitrarily shaped electrode structures. We have applied these computer codes to study some of the issues related to finding the optimum working conditions for streamer corona reactors. Our results show that the radial components of the electron flow and the space-charge field are very important in providing an accurate picture of the streamer morphology, especially near the highly stressed electrode. We are examining the preionization level and other initial conditions necessary for the formation of various streamer morphologies. The effects of electrode structure, voltage pulse characteristics, and gas composition are also being studied.

Our multi-dimensional results bring into question the applicability of 1-D calculations of streamer propagation. We do find that the streamer finds a self-consistent radius which is only weakly dependent of the size of the initial electron distribution. For electrode configurations used with corona discharges, it may not be possible to determine the streamer radius *a priori* and to impose it artificially as is commonly done in quasi-1-D models. As the streamer propagates, the shielding charge in the streamer channel can dominate that at the head of the streamer, implying that a majority of the current goes into shielding the streamer channel and not into directly propagating the streamer head. We observe two types of streamer radii: the first being the equivalent radius of the electron density; the second is the space-charge screening radius, which is much larger. The equivalent radius is the radius which at constant density would contain all the streamer electrons. Space-charge screening in the streamer channel is intrinsically a 2-D phenomenon in which the space-charge is distributed mainly along the surface of the channel. The large shielding radius allows for a significantly larger build-up of charge than can be expected from a 1-D model using an equivalent radius.

Our results indicate four phases in the growth of the streamer radius. In the first phase, the radius expands due to diffusion. The second phase of expansion is governed by the space-charge. In the third phase, the radius remains constant as the streamer propagates. The background electron density during this phase is negligible compared to the electron density at the head of the streamer. The peak space-charge density, electric field and streamer velocity increase linearly with the propagation distance. This behavior is more consistent with a highly-conducting streamer channel than with an insulated streamer head. With the buildup of the background electron density, a fourth phase may be encountered in which the streamer radius rapidly expands. During this phase the streamer velocity is greatly enhanced and there is a reduction in space-charge density and peak electric field at the streamer head.

We show in the figure the early evolution of the equivalent radius in the co-moving frame, for a 0.5 cm gap in N_2 with 30 kV applied potential. The streamer was initiated from a single electron at the cathode. The plus (+) and minus (-) show the directions of the positive and negative streamers. This figure covers the radius evolution up to the beginning of the third phase.

We observe a significant change in the characteristics of the streamer depending on the density of the initiatory electrons. This implies that the early phase of the avalanche formation and its transition into a streamer is important, particularly when the finite risetime of the voltage pulse is taken into account. We also observe a significant difference in the radial structures of the positive and negative streamers, the latter having a larger radial extent and weaker space-charge field. The more localized radial structure of the positive streamer tends to produce higher energy electrons due to the higher space-charge field.



An advantage of our multi-dimensional model is that it is possible to self-consistently calculate the initial evolution of the radial growth of the avalanche and its transition into a streamer. No one really knows how closely adjacent primary avalanches can overlap each other before they inhibit streamer formation. This is dependent upon how the space-charge screening fields of the adjacent avalanches interact. We are attempting to quantify this problem with multi-dimensional simulations.

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THE ROLE OF ELECTRON ATTACHMENT TO GAS MOLECULES IN ELECTROSTATIC PRECIPITATORS

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The efficiency of electrostatic precipitators increases markedly with the voltage that can be applied between the wires and collector plates, provided that electrical breakdown does not occur. Thus the electrical breakdown voltage is a most important quantity determining precipitator performance. The traditional theories for electrical breakdown are the Townsend criterion i.e. $\exp\{(\alpha-\eta)d\} = 1/\gamma$ and the streamer criterion i.e. $\exp\{(\alpha-\eta)d\} = 10^8$. For large distances d of the order of several cm, both theories give the same result that the limiting breakdown field is such that $\alpha \approx \eta$ i.e. that the ionization coefficient α is approximately equal to the attachment coefficient η; γ is the secondary emission coefficient for electron emission at the electrode surface. At low electric fields ionization is zero but becomes very large at high fields. Thus there is a critical electric field for which ionization equals attachment which will correspond to the field for electric breakdown.

However there is a serious problem in that observed breakdown voltages in flue gases, or indeed in air, for corona conditions, are very much lower than the voltage for which ionization would equal attachment. Electrons attach to oxygen, carbon dioxide and water vapor. Electron attachment and ionization coefficients can be calculated or if necessary measured for any mixture of component flue gases. For air it is known that ionization is equal to attachment at a value of $E/N = 120$ Td; E is the electric field strength, N is the gas number density and 1 Td is 1 Townsend or 10^{-17} V-cm^2. On the other hand it is known that electrical breakdown in air for the corona configurations of electrostatic precipitators occurs for average values of E/N of about 20 Td for steady applied voltages, which is a factor of six lower than 120 Td. More recent theories of electric breakdown by, for example, Gallimberti and also Marode, have attempted to explain such phenomena by analyzing the complex processes occurring at the streamer head, and by attributing effects as being due to gas heating.

In the present paper the low average E/N for electrical breakdown in air or flue gases is proposed to be due to the effect of $a^1\Delta_g$ metastable oxygen molecules that are produced in the corona discharge of the precipitator, which would have a strong effect in detaching oxygen negative ions. The critical reaction is:

$$O_2^* + O_2^- \rightarrow 2O_2 + e$$

where metastable oxygen molecules are represented by O_2^*. Thus the effective attachment rate is significantly lowered by the presence of metastables.

Cross sections for the excitation of $a^1\Delta_g$ oxygen molecules are known as a function of electron energy. Calculations have been made of electron energy distributions as a function of E/N by solving the Boltzmann transport equation for air and also for air with various proportions of water vapor. Thus the excitation coefficient for metastable production has been calculated as a function of E/N. Similarly the ionization and attachment coefficients have been calculated as a function of E/N. Momentum transfer and inelastic cross sections for nitrogen, oxygen and water vapor have been taken from the literature.

Using these coefficients, rate equations have been formulated for ionization, two and three body attachment, recombination, and also for the production of metastables, metastable detachment and metastable quenching. Metastable detachment and quenching coefficients were taken from the literature. The time dependent behaviour of the particle densities for electrons, positive ions, negative ions and metastables was then calculated for various values of E/N and for various initial conditions of particle densities. For these calculations it was necessary to assume an effective ionization coefficient at very low E/N: a value of $\alpha/N = 10^{-22}$ cm^2 was chosen for E/N = 20 Td and interpolations made to merge with known values at higher E/N i.e. 10^{-20} cm^2 at E/N = 70 Td.

From the calculations it is found that the effect of the metastables is to lower the breakdown voltage from 120 Td to approximately 20 Td. It is possible to derive an analytic relationship between attachment, ionization, metastable and recombination coefficients to give the critical minimum value of E/N defining the breakdown voltage for any given flue gas mixture.

These methods have been applied to calculate the sensitivity of the breakdown voltage to water vapor. The calculations predict that 1% by volume of water vapor will increase the breakdown voltage by 11% which is in good agreement with experimental results of 10.5%. This sensitivity of the breakdown voltage to water vapor is due to (a) the high quenching rate of metastables by water vapor (b) the high efficiency of water vapor as a third body for electron attachment to oxygen and (c) the very high rotational and momentum transfer cross sections of water vapor.

The theory gives an indication of how to improve precipitator behaviour by adding minority gases. A gas which is strongly electron attaching would increase the breakdown voltage and thus precipitator efficiency.

ELECTRON DATA BASE NEEDED FOR DISCHARGE MODELING IN FLUE GAS TREATMENT

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The use of pulsed corona discharges for the removal of certain polluting agents (NO_x, SO_2, etc.) from industrial flue gases is now under investigation in several laboratories in the world. The role of corona discharges is to produce energetic free electrons which ionize, excite and dissociate flue gas molecules. Certain radicals (mainly OH, O) produced through these processes can favour, following more or less complex chemical reactions, first the transformation of polluting agents [1] and then their removal from flue gases using classical methods [2]. Optimization of the efficiencies of such chemical reactions needs, in particular, a better knowledge of corona discharge characteristics under, for example, different pulsed voltage stresses [2].

Modeling of pulsed corona discharges, which is a necessary complement to experimental investigations, can contribute towards improving the plasma device efficiency. Classical fluid models are generally based on the following macroscopic equations:

- Electrical circuit equations,
- Hydrodynamic conservation equations for transport of charged carriers (electrons, positive and negative ions),
- Evolution equations of heavy particles corresponding to plasma chemistry,
- Poisson equations describing space charge electric field.

Discharge modeling is nowadays not really limited by numerical constraints but mainly by the knowledge of reaction kinetics and also by the lack of data base such as heavy particle reaction rates or electron transport coefficients. The electron data necessary for fluid models are drift velocity, longitudinal and transverse (for 2D geometry) diffusion coefficients, ionization and attachment coefficients. Experimental determinations for electron transport coefficients in flue gas are rather sparse and can be found in the literature only for some specific flue gas compositions [3]. It is well known that Boltzmann equation analysis constitutes an interesting alternative for electron transport coefficient determinations, whatever the composition of the flue gas considered. Therefore, the aim of the present contribution is to analyze, from a multi-term numerical solution of Boltzmann equation [4], the electron distribution functions and associated transport coefficients. The most important electron-molecule collisional processes (elastic, inelastic and super-elastic) are considered and corresponding collision cross sections for the major component of flue gases from coal or oil fired power plants (N_2, O_2, H_2O, CO_2) are analyzed in the light of a classical method of cross section fitting. Then, the influence of the flue gas composition and also the dependence of, particularly, electron attachment coefficients on background gas are emphasized. Finally, the consequence of these transport coefficient dependencies on discharge parameters (distribution of space charge electric field, charged particle densities, current densities, etc.) is analyzed using a fluid model (based on classical macroscopic equations solved from a powerful finite element scheme with non-uniform meshes) and coupled to microscopic Boltzmann equation for electrons.

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SWARM DETERMINATION OF ELECTRON-MOLECULE CROSS-SECTIONS IN SOME HYDROCARBON GASES SUCH AS METHANE, PROPANE AND ISOBUTANE

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The study of hydrocarbon vapours is usually assumed to be important mainly in connection with combustion problems. However, as most of these gases are emitted from various industrial devices, they may be considered as major pollutants, so a good knowledge of their physical and chemical properties becomes necessary for a better prediction of their effects. It is well known for example that propane is mainly ejected by cars and that volatile organic compounds, like toluene, are emitted from the chimneys of factories producing paint. In order to develop a discharge reactor to eliminate most of these organic compounds, modeling may be necessary to improve its basic properties. In this case, since many different molecules may appear during the discharge process, basic data describing the electron-molecule or ion-molecule interactions with hydrocarbon vapours, usually mixed with air, are a prerequisite.

Unfortunately, for most of these gases, knowledge of basic data is very poor. In this communication our aim is to show, for electron-molecule interactions, how the swarm method in connection with other procedures may be very successful in determining electron-molecule cross-sections, even in the case where few experimental or theoretical cross-sections are available.

Our study focuses on three important molecules, i.e. methane, propane and isobutane, in order to emphasize the increasing difficulty associated with the rise in the complexity of the structure of these molecules.

The simplest being methane, the results were much more accurate compared to other molecules. However, due to the large number of experimental swarm parameters available together with other experimental data, coming from particle detector experiments, a very accurate set of cross-sections can also be obtained for propane. The same was obtained for isobutane, but, due to the very complex structure of the molecule, the cross-sections were less accurate.

An application of these cross-sections to the calculation of swarm parameters in mixtures of gases, such as a mixture of air with propane or methane, is given.

INFLUENCE OF ACTIVE RADICALS ON NO/SO_2 REMOVAL FROM FLUE GASES IN CORONA DISCHARGE INSTALLATIONS

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Most existing theoretical and experimental studies in the field of flue gas cleaning consider only the general process characterized by the degree of removal of NO/SO_2 related to the electrophysical parameters of the corona discharge.

The pulsed corona discharge installation of the Eindhoven University of Technology (EUT) was taken as a model for this research. The analysis was made for two flue gas mixtures: typical coal combustion flue gas (74% N_2, 5% O_2, 15% CO_2, 6% H_2O) and the typical mixture of the EUT installation (70% N_2, 6% O_2, 8% CO_2, 16% H_2O). The initial concentration of NO was set to 400 ppm, the initial concentration of SO_2 to 1000 ppm. The initial concentration of active species (OH, H, e^-, N_2^+, N_2^*, O^-, O_2^-, O_3^-, O_4^-, O, O_2^*) was varied near the expected characteristic value for the experimental low current corona discharge installation. The default concentrations were: OH and H: 1% of the concentration of H_2O; e^-: 2.1×10^{14} cm^{-3}; N_2^+: 2.1×10^{14} cm^{-3}; N_2^*: 6.8×10^{14} cm^{-3}; O^-: 2.4×10^{11} cm^{-3}; O_2^-: 3.8×10^{12} cm^{-3}; O_3^-: 1.0×10^{9} cm^{-3}; O_4^-: 5.1×10^{11} cm^{-3}; O: 2.1×10^{15} cm^{-3}: O_2^*: 5.0×10^{15} cm^{-3}. The concentration of OH and H has been vacated from 0.1% of the concentration of H_2O to 5%; the concentrations of the other particles have been vacated to zero.

Based on the results of these investigations, the following conclusions can be made:

1) Under conditions characteristic for low current corona discharges the NO removal is 34% (of which 15% is by conversion of NO to NO_2); the SO_2 removal 5%.

2) Under these conditions the main part in the NO/SO_2 cleaning process is played by OH radicals (for NO removal 93%-96% of total cleaning; for SO_2 removal more than 95%). The characteristic time of this process is 10^{-4} s.

3) Under these conditions the concentration of produced O_3 remains small (typically 10^{14} cm^{-3}), due to the small initial concentration of active oxygen species (O, O_2^*, O^-, etc.). Therefore O_3 plays only a small part in NO removal (3%-7%). The characteristic time of this process is 10^{-2} s.

*guest student from EUT.

THE EFFECT OF CLUSTERS AND HETEROGENEOUS REACTIONS ON NON-EQUILIBRIUM PLASMA FLUE GAS CLEANING

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Heterogeneous reactions in droplets and clusters are essential in the evolution of the chemical composition during plasma cleaning of flue gas from SO_2, NO_x, H_2S and VOC's. These reactions are of concern because such particles form fast in high pressure systems, and there is also the possibility of effective, in particular chain, chemical reactions in aerosols and clusters. Furthermore, most of the experimental data obtained in electron beam and pulse corona discharge could not be explained without taking into account heterogeneous processes. Unfortunately up to this moment there have been no detailed investigation of these effects. The full modeling of SO_2, NO_x, H_2S and VOC purification in heterogeneous non-equilibrium plasma is presented in this work. The peculiarity of the model consists also in the possibility to investigate the transition regime of non-equilibrium plasma generation between the linear region when ion, radicals, excited molecules and atoms react preferably with the matrix gas or admixture, and the non-linear one when active particle-active particle reactions predominate. This transition regime seems to be profitable for purification processes because of the cooperative effect of the different types of active particles in this case. The main objective of our approach and modeling is to find the optimum regime of plasma generation (specific power, humidity, etc.) for essential decreasing of purification energy costs, taking into account the heterogeneous effects.

The elaborated model takes into account the following types of chemical decomposition reactions: gas phase reactions including reaction of excited particles, cluster chemistry, droplet phase oxidation reactions, and surface catalysis. The structure of the modeling program is based on physical-chemical processes time scale and includes four main codes: non-isothermal gas phase and cluster kinetics; non-uniform kinetics (including transfer processes) for droplet and boundary layer region; kinetics of droplet formation, coagulation and evaporation; and modeling of discharge and e-beam active particle production. In the particular case of flue gas cleaning from SO_2 and NO_x, the chemical code includes 520 gas-phase and 160 liquid-phase reactions. For effective investigation of such type of complex systems we also use two auxiliary programs. The first one - Doctor Chemy code - is used for search in database and determination of unknown reaction rate coefficients. This program is based on a set of independent theories and permits the calculations of the value and accuracy of rate constants for all types of reaction under consideration (regular chemical reactions, plasma chemical reactions, reaction of excited particles, etc.). The second one is the sensitivity analysis code for the calculation of total accuracy of the results obtained and for finding out the main physical-chemical mechanism of the process.

Our modeling confirms the essential role of heterogeneous chemistry in cleaning processes and the advantage of the boundary (linear - nonlinear) regime of plasma generation. In particular, it is possible to elucidate the following effects.

It was shown that it is possible to significantly reduce the SO_2 oxidation energy cost to 0.3 eV at a definite range of electron-beam current density and air humidity. This effect can be realized because of ion-molecular chain oxidation mechanism in clusters and it is connected with the formation of the negative ion $SO_4^-(H_2O)_n$. This cluster has peroxide structure and very high oxidation activity and for this reason it is the main chain promotion agent. Negative-ion chain effect can be realized in the transition regime of plasma generation. Low specific power region is not profitable because to the low excitation level. High specific power is also not profitable because of the rapid recombination (with respect to ion-molecular chain propagation reactions) recombination of the ion.

It was shown that spraying of relatively small amount of water droplets of definite size permits the organization of very effective SO_2/NO_x cleaning process: to attain low SO_2 oxidation energy costs; to substitute NOx oxidation for NO_x reduction; and to simplify significantly the product collection. In this case SO_2 oxidation proceeds as a result of negative-ion chain processes in droplets, initiated by the active radicals from the gas phase. On the other hand, NO is oxidized to NO_2 in the gas phase and after that effective NO_2 quenching with respect to back reactions occurs because of NO_2 absorption by droplets. At the optimum conditions NO_2 in droplet plays the role of the oxidizing agent with respect to S(IV) and in the result we obtain S(IV) and N_2 as products. Droplet chemistry can also explain the results of the recent electron-beam experiments made by Hamba *et al.* when NO_x removal increase from single to double and triple irradiation even without the installation of an intermediate filter as in the case of KFK (Germany). We have shown also that the heterogeneous system is very effective in the cleaning of air stream from H_2S and VOC's.

All main results obtained in the modeling, in particular the reduction of SO_2 oxidation energy cost by ion cluster chain reactions and the effective heterogeneous cleaning of air stream from H_2S and VOC's, were confirmed by appropriate experiments made in pulse and continuous electron beam, and heterogeneous barrier discharges.

Now we will develop our program to investigate the cooperative effect (simultaneous influence of discharge and UV-radiation; electron beam and ozone; etc.) in purification processes.

CHEMICAL KINETIC DATA FOR MODELING NON-THERMAL PLASMAS

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All fundamental research on non-thermal plasma chemical processing implies the existence of a model. How valid are the models and how useful are they in process scaling? Does agreement of a model with observational parameters tell us anything about the process, or is this simply an exercise in curve fitting?

Modeling provides a means for simulating the behavior of complex systems and thus avoids the need to use direct testing methods. The goal of a chemical kinetics model is to describe a complex system in terms of a set of single-step elementary reactions, each of which is characterized by a rate expression which is a fully transferable property of the reaction. A chemical kinetics model is but one part of a more general model describing the chemical and physical properties of the system.

The ultimate chemical kinetic model would include rate expressions for every possible electronic, vibrational, rotational and translational configuration of the system. There is little or no prospect of that kind of microscopic model ever becoming a reality. There are no diagnostics available to describe the system at that level of detail, and no database extant or on the distant horizon to provide the necessary input to the model. Fortunately, that kind of model is not necessary for most practical applications. Almost all systems of interest can be treated in terms of some kind of local or partial thermodynamic equilibrium. This is of vital importance in terms of modeling, since the only significant sources of kinetic data are for thermal systems.

In general, thermal plasmas are thermodynamically determined, while low temperature non-thermal plasmas are kinetically determined by reactions of neutral atoms and molecules, their ions, and the interactions of gas phase species with surfaces. The key questions are which reactions lead to the observed final products and conversely which reactions cause their destruction, what properties of the products (e.g., bond strengths) determine stability under plasma conditions, and how reactant and product distributions may be enhanced or altered.

In the case of non-thermal plasmas, non-equilibrium effects may have to be treated explicitly since the gas and electron temperatures may diverge. Energy transfer in electron-atom or electron-molecule interactions can lead to population of higher rotational, vibrational or electronic states. While rotational relaxation is probably sufficiently fast to equilibrate the rotational population, that is not necessarily the case for the vibrational or electronic states. These processes must be characterized at the elementary reaction level. Their importance will depend on the relative rates of reaction of the excited states compared to the ground states, and their steady state population. Rate data for vibrationally or electronically excited species exist in some cases and are experimentally accessible in others. If there is no indication that excited state chemistry is important, the correct starting point is the fully thermalised system.

The design of a model should take into account the existing body of chemical kinetics data, theory, and experience, and the available evaluated databases. These will be discussed.

A model should include all possible species and all possible reactions. For each reaction it should provide a recommended rate expression applicable over the range of temperature and pressure encompassed by the model, and in the absence of literature data provide an estimate of the rate expression using theoretical or empirical methods. There is a hierarchy of reactions in any system and many reactions can be readily shown to be unimportant and excluded from further consideration. Only those reactions which determine the properties of the system need to be included in the model. The important thing initially is to consider all possibilities and then simplify the model as much as possible. Also, since a model is built through a process of iteration, in its initial form it is not necessarily or even likely to be a correct representation of the chemistry. It is state-of-the art at any given time. It provides a common point for comparison of model calculations, and the identification of critical data needs. Existing databases for atmospheric and combustion chemistry can provide a basis for modeling some of the plasmas of practical interest. However, for plasmas involving organo-metallic compounds, metals and their oxides, carbides, halogens, etc., data are rare and of uncertain quality.

These factors will be discussed with reference to selected non-thermal plasmas.

TECHNOLOGY DEVELOPMENTS

PLASMA ARC PROCESSING OF SOLID AND LIQUID WASTES

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The processing of solid and liquid wastes is well suited to plasma treatment as it can be omnivorous as related to a wide range of feed materials.

The equipment being discussed in this presentation is the Plasma Centrifugal Furnace (PCF), which has been configured to enable treating a broad range of toxic materials. The furnace employs a hollow electrode plasma torch, which is operated in the transferred mode for pyrolysis and vitrification of the waste stream.

A brief description of the transfer of metallurgical processing experience to toxic waste applications will be discussed along with material handling and maintenance considerations.

ENERGIZATION OF PULSE CORONA INDUCED CHEMICAL PROCESSES*

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Pulse corona is a suitable means for generating low temperature plasma used for inducing chemical reactions leading to the removal of gaseous pollutants. Energy consumption is a key factor of the process and it must be reduced as much as possible. This reduction can be achieved:
i) by optimizing the energy efficiency of the circuit used for producing the corona discharge;
ii) by enhancing the chemical process by chain reaction mechanisms.

The optimization of the energy efficiency in producing the corona discharge process depends on the type and design of the pulse voltage generator circuit together with the electrode arrangement.

The possibility to promote a chain reaction mechanism in heterogeneous phases seems to depend an the achievable power density of the pulse corona discharge, which, in turn, depends on the pulse voltage shape and electrode arrangement.

The paper will report on the results of a recent investigation on positive pulse corona discharge in wire-cylinder and wire-plate electrode arrangements using atmospheric air. The applied voltage was formed by a DC base voltage on which voltage pulse of very short duration were superimposed. Large bandwidth current and voltage measurements allowed the determination of the corona power functions and the empirical modeling of the dynamic impedance of the pulse corona discharge.

Criteria for optimizing the energy efficiency and for achieving the largest pulse corona discharge power density are also presented.

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DESIGN AND INITIAL TESTING RESULTS FROM THE REPETITIVE HIGH ENERGY PULSED POWER (RHEPP) PROJECT*

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Pulsed discharges or electron beams are being considered for disposing of many types of gas pollutants. Implementation of these techniques will require either high average power eletron beam accelerators or high average power pulse generators. In the RHEPP Project, we are developing a technology base that should allow fabrication of high power systems with components that have a mean time between failure of several years and could satisfy these pollution control needs.

The RHEPP module consists of the following major subsystems: 1) a multistage, magnetically switched, pulse compressor that has an input from a 120 Hz, 600 kW alternator and produces 250 kV, 1 μs pulses 2) a 60 ns pulse compression unit that uses magnetic switches and pulse forming lines to reduce the pulse duration from 1 μs to 60 ns, and 3) a 2.5 MV, a 10 stage inductive voltage adder with an electron beam diode.

The first phase of this module is in final assembly. In this phase, 400 kW of power will be produced by the pulse compression units. Forty percent of this power will be delivered to a 4 stage, 1 MV adder and electron beam diode. The remaining power will be either delivered to a resistor or be available for experiments. A description of the system and test results from the initial stages of the pulse compression will be presented.

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HIGH AVERAGE POWER MODULATOR AND ACCELERATOR TECHNOLOGY DEVELOPMENTS AT PHYSICS INTERNATIONAL

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Pulsed systems operating at high average power have applications in flue gas clean-up, in reducing greenhouse gases, in atmospheric modification, in medical waste processing and in water treatment. For these applications, the pulsed power system can be the driver for a corona discharge, an electron beam diode, a bremsstrahlung diode or microwave cavity.

At Physics International, we have developed a state-of-the-art modulator and accelerator as a microwave source but similar designs can be used for pulsed corona or electron beam applications. The system at PI is called the compact linear induction accelerator (CLIA), and its operational parameters are 750 kV, 10 kA, 60 ns and 200 Hz. CLIA was designed to operate in a burst mode to investigate the physics of high repetition rate high power microwave cavities and it has been demonstrated to run at 250 Hz for a second and for 50 seconds at 100 Hz. A peak repetition rate of 1000 Hz can be produced.

The CLIA system [1] consists of (from the load back to the mains) a ten-cell linear induction voltage adder, ten magnetically switched water insulated pulse forming lines (PFL's), a two-stage Magnetic Compression Unit (MCU), and thyratron-switched Intermediate Energy Store (IES), and Command Resonant Charge (CRC) units. A linear induction accelerator system was used because it allows all pulse compression to be done at moderate voltage (40 to 150 kV) and then uses the accelerator structure to add parallel voltage pulses into a single high voltage output (750 kV). Nowhere except at the load does a voltage of higher than 150 kV appear. This allows the switching to be done at moderate voltage and the use of hydrogen thyratrons and magnetic switches is possible. CLIA has been used to drive L-band magnetron and relativistic klystron microwave sources. In these tests, up to 6.3 kW of average microwave power has been demonstrated in a short burst; all at the GW peak power level. [2]

CLIA is the ideal technology to be adapted for many of the applications listed above. For example, focusing on flue gas conditioning, CLIA can be used directly to produce electron beams for flue gas irradiation or the modulator, and MCU can be adapted for the pulsed corona technique.

The pulsed corona technique [3] is more attractive due to its higher efficiency, lower retrofit cost, and decreased voltage/X-ray safety issues. A pulsed corona technique will also allow smaller modules so that it is applicable to small and large power plants. In this paper, we will present designs for a CLIA based system to cover the range of parameters for the pulsed corona technique that is 100 to 200 kV, few hundred Hz RPF, 500 to 1000 J per pulse and < 1 µs pulsewidths. These can be covered by variations in the MCU and the use of PFL's to control the pulsewidth. We will also discuss the technology issues associated with optimizing the pulsed corona process, and constructing such a high average power system with long lifetime and low lifecycle costs. Finally, we will briefly discuss the application of the PI CLIA technology to other environmental processes.

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DEVELOPMENT OF THE ELECTRON BEAM DRY SCRUBBING OF FLUE GAS UTILIZING HPTA TECHNOLOGY

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Large coal fired facilities contribute significantly to acid rain and other pollution problems through the emission of SO_2 and NO_x. The New Clean Air Act currently mandates significant reduction in SO_2 and will probably require significant NO_x reduction after 1995. Thus, utilities which rely on high sulfur coal will be severely affected.

Electron Beam Dry Scrubbing (EBDS) by irradiation of flue gases is the most promising method for simultaneous removal from high sulfur coal of SO_2 and NO_x in a single step. It is a dry process whose by-product is a fertilizer of commercial value. In spite of recent advances in EBDS technology to improve process efficiency and by-product collection, there are still significant obstacles which prevent the wide scale application to coal fired facilities - the size, cost, and average power of current electron beam technology.

We have performed a conceptual design of a high average power (1.5 MW) electron beam generator using the High Power Transformer (HPTA) technology that satisfies the size, cost and average power requirements for the EBDS process. We developed a number of innovative technical solutions to the design problems associated with the various pulsed power subsystems to arrive at a reliable, cost effective, high power generator. We will discuss the electron beam generator requirements and design issues for the slow power conditioning system, the saturable reactor modulators, HPTA and electron gun.

PARTICIPATION OF THE INSTITUTE OF NUCLEAR PHYSICS (NOVOSIBIRSK) IN PROGRAMS OF ELECTRON BEAM FLUE GAS TREATMENT AND DEVELOPMENT OF HIGH POWER ACCELERATORS

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The ELV type accelerators of our Institute have found applications in ecological projects due to their high efficiency and desired high power. Now we are ready to deliver high voltage direct current (ELV-type) accelerators with the following parameters:

- Energy (E = 0.2 - 2.5 MeV);
- Power (P = 100 kW);
- Current (I = 100 mA).

Table 1 lists ecological ELV-based devices that are operating and those that are being developed:

Table 1 Ecology projects based on ELV-type accelerators

OPERATIONAL:

N	Location	Designation of Project	Type of Installation	Date of Realization
1	Synthetic rubber factory Voroneg, Russia	Treatment of waste water with surfactant	Industrial	1984
2	Metallurgy plant Lipetsk, Russia	Development of technology for purification of gases from SO_2 and NO_x	Laboratory	1988
3	Thermal Power Station Kaweczyn-Warsaw Poland	Development of technology for purification of gases from SO_2 and NO_x	Demonstrative, experimental	1990
4	Tin plant Novosibirsk, Russia	Cleaning of fume gases from SO_2	Experimental industrial	1991
5	NKK Corp. Tokyo, Japan	Development of technology for purification of gases from SO_2 and NO_x	Experimental	1992

UNDER CONSTRUCTION:

N	Location	Designation of Project	Type of Installation	Date of Realization
1	SAMSUNG Heavy Industries Co. Seoul, Korea	Development of ecology technologies	Experimental	1993
2	Electro Power Station Donbass, Ukrania	Cleaning of fume gases from SO_2	Experimental industrial	1994
3	Sewage works Lebiage, Russia	Purification of waste waters	Experimental industrial	?
4	Textile mill factory Riga, Latvia	Purification of waste waters of paint production	Industrial	1993
5	Natural gas plant Orenburg, Russia	Purification of natural gas after Klaus installation	Industrial	?
6	City sewage works Petrodvorets, Russia	Purification of waste waters	Experimental industrial	?

For industrial plants, 200 kW and higher accelerators are required. At present, we are developing two types of higher-power accelerators. The first is based on beam extraction through a foil. For this purpose, an extraction device with two foil windows has already been designed.This will make it possible to extract up to 200 mA. It will be the accelerator whose design is typical for ELV type accelerators.

In the second accelerator with focused beam extraction, differetial pumping is used. A high-voltage rectifier and an accelerating tube are connected by a high-voltage feeder. The accelerating tube is introduced in the longitudinal magnetic field, low at the cathode and increasing to the extraction device. The results which were already reached at this facility are as follows:

$$E = 600 \text{ keV},$$
$$P = 360 \text{ kW}.$$

However, this operational mode is not quite stable. Our urgent task is to increase the power and to reach the stability in operation.

RESEARCH TO IMPROVE THE EFFICIENCY OF PULSED POWER SWITCHES AND BEAMS FOR HIGH AVERAGE POWER SYSTEMS FOR POLLUTION CONTROL

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This presentation describes research activity to develop improved, efficient pulsed power switches and electron beams for high average power systems. Improved efficiency is perhaps the critical issue in the development of high average power, long life, high voltage and high current systems for the production of coronal discharges and/or electron beams for pollution control. These systems must operate with long life, require minimal maintenance, and work well within limits related to the fraction of produced power available for the pollution control system. Such systems have fundamental efficiency limits resulting from component limitations - and the effect of component limitations on the system or modulator configuration - an example being the limitation on efficiency derived from the forward drop and commutation losses of a switch, and the additional limitation on system efficiency resulting from required additional components, such as transformers or magnetic pulse compression, necessary to achieve desired voltages, currents and pulse shapes.

In order to develop improved devices, we have 1) investigated the underlying physics responsible for the most dissipative aspects of the device, and 2) applied these results to the *development of improved switches* and beams. The most important physics limitation is often the cathode emission process.

We will describe three devices, including a plasma-based pseudospark-type pulsed power switch, a hollow cathode electron beam source, and an electron source based on a super-emissive cathode. In addition, the physical processes responsible for the remarkable switching and emission properties will be discussed.

We are developing a new plasma switch capable of making pulsed corona discharge treatment of flue gases economically and technically feasible. The switch will be a simplified design of the superemissive cathode back lighted thyratron (BLT) or pseudospark switch [1]. These switches have demonstrated high voltage, high repetition rate characteristics of thyratron switches while operating with high currents, low inductance and simple structures characteristic of spark gaps. In addition the BLT switch can be triggered with a low, ~10 V electrical pulse or optically by UV light sources. This switch is fundamentally different in operation from other gaseous discharge switches, such as thyratrons, hollow cathode switches, and spark gaps. It is a super-emissive cathode switch, (loosely defined as one which produces uniform current emission ≥10,000 A/cm^2 from a macroscopic, rather than microscopic area ~1 cm^2) originating from a refractory metal, hollow electrode. The current emission characteristics are very large in comparison with conventional heated thermionic cathodes.

The physical process responsible for this emission includes two important phases. The release of starting electrons inside the hollow cathode initiates a transient hollow cathode discharge. During this growth phase of the discharge, before the plasma is fully formed, a transient high voltage remains across the electrodes, and an electron beam is produced that passes through the anode aperture. The cathode then makes a transition to a different phase, the superemissive phase. This phase has extraordinary emission properties, including production of current densities 10^4 to 10^5 A/cm^2, generated over a macroscopic area ≈1 cm^2.

The hollow cathode plasma can be controlled for applications including electron sources and beams. These beams are reported to have kA peak currents and very good emittance and brightness properties - we have observed 55 mm-mrad and 2×10^{11} A-m^{-2}-rad^{-2}, respectively at 20 kV with ≈1 kA beam current. Variable pulse-length electron beam generation was achieved by modification of circuit parameters that control the hollow cathode discharge. With 75 mTorr Ar and 20 kV applied voltage, the electron beam made a transition through two distinct phases; first with higher current and fast-decaying voltage (from 20 kV to 2 kV), second with lower current and slowly-varying voltage (≈2 kV).

A robust, high current electron beam, produced operating in the superemissive mode, is also to be discussed. We have observed super-emissive electron beam current of >150 A, with electron energies of several hundred eV and the electron beam has the duration of the discharge pulse. A simple differential pumping scheme has been used to demonstrate that the extraction of electron beam into low pressure (<7 mTorr) or vacuum is practical. These devices are simple, robust, and the electron sources are compatible with a plasma environment.

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POWER CONDITIONING FOR EFFICIENT, EFFECTIVE REMOVAL OF NO_X/SO_X AND TOXIC MATERIALS FROM EFFLUENT GASES

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Pulsed corona discharge treatment of flue gases for effluent control has the potential for effective removal of SO_X, NO_X and various other toxic materials. Pulsed plasma processing has been demonstrated to be an effective method for removing NO_X, SO_X and soot from power plant effluent gases and diesel engine exhaust, with a key issue being implementation of an efficient, robust, low maintenance pulsed power system. This method requires repetitive pulsed power systems which have been difficult or expensive to operate, inefficient, and suffer from other limitations as well, hence are a key limitation to the feasibility of the method. A robust, economical, efficient pulsed power method is described. In this work we are developing novel pulse modulator concepts with higher efficiency and more reliable construction. The approach is based on a new innovation in repetitive switching, the super-emissive cathode switch (SEC). The SEC switch has several versions including the pseudospark and the back lighted thyratron (BLT), and has demonstrated high voltage, high repetition rate and long life characteristics of thyratron switches while operating at higher currents, lower inductance and simpler structures that are robust and more suitable for high voltage operation in industrial applications. The SEC switch based modulators will be more efficient and economical than presently available, requiring considerably less peripheral circuitry. Preliminary results of this modulator development will be discussed including the performance of this type of modulator at the operating requirements specified by engineers implementing the pulsed corona method.

A LONG LIFE, HIGH REPETITION RATE ELECTRON BEAM SOURCE

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Large emitting area, pulsed, moderate repetition rate electron beam sources are potentially useful in gaseous pollution control if they can demonstrate suitable longevity and reliability. A multikilohertz electron beam source is now described which has a potential lifetime of at least $> 10^9$ shots and should be scalable, in terms of cross sectional area and voltage. This device was developed for an x-ray preioniser for incorporation into a 1 kW output power industrial excimer laser. At present the source characteristics are: emitting area 1 cm x 40 cm, peak voltage 90 - 100 kV (depending on diode impedance), current density $\approx$ 10 A cm^{-2}, electron beam risetime 100 ns with FWHM of 80 ns and maximum repetition rate 2.4 kHz.

The device is a highly evolved form of corona plasma cathode; on application of a fast rising voltage pulse across two electrodes separated by a solid dielectric a corona discharge is initiated on one side at the dielectric-vacuum-electrode triple point. The discharge spreads out across the dielectric surface removing and ionising surface materials - adsorbates, dielectric and electrode material. It is from the resultant plasma that an electron beam can be extracted by means of an accelerating voltage. In order to achieve a long cathode lifetime the contribution of the dielectric and electrodes to the plasma and the dielectric stress must both be minimised. This is achieved by using a low plasma generating voltage, cooling the dielectric, using low erosion design electrodes and careful regulation of the background pressure which is directly proportional to the adsorption rate of oil and water vapours etc.

The driving circuitry consists of 4 nF, command charged at 30 kV and thyratron switched into a 1:3.5 turns ratio pulse transformer. The output from this is taken to the cathode via an oil/vacuum feedthrough. The whole of the circuitry is immersed in recirculating, continuously cooled oil. The current to the cathode is measured using a coaxial resistive shunt and the voltage by a differential field probe, these diagnostics were chosen as being particularly suitable for monitoring sustained high repetition rate operation.

The cathode was run at 2 kHz for 28 hrs, the longest continuous run being 5 hrs and then the repetition rate was raised to 2.4 kHz and operation maintained for a further 6 hrs. A total of 2.5×10^8 shots was accrued and then the system examined for wear. The dielectric surface was slightly roughened but no measurable erosion (< 10 μm) had taken place, the electrodes were uniformly worn by 0.3 mm along their length. As the useful electrode width in the present design is $\approx$ 5 mm the present lifetime limit was estimated to be 3 - 4×10^9 shots (i.e. 500 hrs at 2 kHz, 5000 hrs at 200 Hz).

In order to be useful in gas processing the electron beam voltage should be $\geq$ 300 kV - the cathode should be capable of operating at these potentials given a suitable driving circuit. With further modifications to the electrode structures even longer lifetimes ought to be possible. The cathode design is readily scalable and so this type of electron beam generator could, with development, become a viable candidate for plasma gaseous pollutant control.

GENERATION OF ELECTRON BEAM FOR TECHNOLOGICAL PROCESSES

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The results of the experimental study of the electron beam generated by a plane cathode in the high-voltage glow discharge [1-3] are summarized in this paper. The aim of our work was to obtain information about the electron beam which could be used for the optimization of the electrode system for new technological processes decreasing the negative impact of classical technologies on the environment.

All the experiments were performed in air atmosphere in pressures of several Pascals.

The electron beam was emitted by the plane cathode cooled by water. The anode (the copper target cooled by water) served as a collector of electrons. During some measurements, the central electrode (copper tube 8 mm in diameter cooled by the water flowing through it) was used to replace the annealed wire. However, the majority of the measurements were performed without it.

The cathode was made with an aluminum cylinder with the circular groove of radius 25.5 mm milled in it. The cathode was surrounded by the steel shielding which was not grounded.

The material of the cathode emitting surface has the decisive influence on the volt-ampere characteristics of the discharge; this fact is caused by the dependence of the secondary emission coefficient γ on the material of the cathode. In experiments described here the cathodes from aluminum, copper and steel were studied; for the coefficients γ of these materials the relation holds

$$\gamma_{Al} > \gamma_{Fe} > \gamma_{Cu}$$

From the experimental results it is obvious that the aluminum is the most suitable material for the cathode.

The main objective of our experiments was to determine the shape, the geometrical dimensions and the focal distance of the electron beam. To realize it, the probing of the electron beam by the thermocouple probe and current probe has been used. The obtained results have been also compared with the photographs of the beam.

As it follows from the obtained experimental results, both methods of probing the beam could be used when the shape and the focal distance of the electron beam from the plane cathode are to be determined.

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DC GLOW DISCHARGE WITH FAST GAS FLOW FOR FLUE GAS PROCESSING

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DC glow discharge in an air flow is known to be sustained at a pressure usually not higher than 70 Torr. By creating special electrode configuration we realized a dc glow discharge at an air pressure up to 2 atm. Having this discharge it is of great interest to employ it to the problem of control of harmful pollutants in a flue gas.

Measurements of electric discharge characteristics demonstrated that most part of electric current is carried by electrons. Electrons have an average energy of the order (2-5) eV. Hence the effectivity of this discharge in producing chemically active species like atoms and radicals is high enough. An average electric power density in the discharge under investigation is about two orders of magnitude higher than in barrier or corona discharge.

To verify this discharge as an efficient source of the chemically active species the special experiments were carried out. We had employed our discharge in the dried air to produce the ozone which has many applications in industry as the very strong oxidizer. The ozone concentration produced in the discharge reached the value 0.05% at the energy cost 12 kWh per kg of ozone (or 21.6 eV/mol).

The capability of the discharge to activate the gas was checked also by its effectivity to oxidize some hydrocarbons like butane or propane. The experiment demonstrated that the energy cost for this process in the discharge is the third of that for the thermal oxidation.

The experiments for air cleaning from SO_2 were carried out on a laboratory scale installation with an artificial gas. This gas consist of humid air (with variable humidity) and small special admixtures SO_2 and NH_3. SO_2 removal efficiency up to 20% was achieved without NH3 injection for initial SO_2 concentration 1000 ppm at the reduced energy deposition 30 J/g. By injection of stoichometric of ammonia the whole removal efficiency was obtained up to 96%.

The processes of plasmas assisted NO removal were studied on the flow of the real stack gas at the output of the local boiler fired by the natural gas. This flow did not contain a measurable amount of SO2 and the concentration of nitrogen oxides equalled to 65-75 ppm. The NO removal efficiency was studied as a function of the gas flow velocity, the energy deposition, the moisture content and ammonia concentration. The NO removal efficiency up to 70% was achieved at the reduced energy deposition 40 J/g.

So, the results of SO_2 and NO removal from a polluted gas by dc glow discharge treatment demonstrated this method to be very promised for industrial applications.

In this talk the results of modeling of this discharge in a dry air will be presented. The role of electronegative components in the mixture will be discussed.

AUTHOR INDEX